

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-142212

(43)Date of publication of application : 25.05.2001

(51)Int.Cl. G03F 7/039
G03F 7/004
H01L 21/027

(21)Application number : 11-321347

(71)Applicant : FUJI PHOTO FILM CO LTD

(22)Date of filing : 11.11.1999

(72)Inventor : AOSO TOSHIKI
SATO KENICHIRO
KODAMA KUNIHICO

(54) POSITIVE PHOTORESIST COMPOSITION**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a chemically amplified positive photoresist composition having high sensitivity, high resolving power and good adhesion to a substrate and ensuring improved edge roughness of a pattern.

SOLUTION: The positive photoresist composition contains (A) a compound which generates an acid when irradiated with active light or radiation, (B) a resin which is decomposed by the action of the acid to increase its alkali solubility and (C) a solvent containing 60-90 wt.% solvent (a) based on the entire solvent. The solvent (a) is propylene glycol monomethyl ether acetate, propylene glycol monomethyl ether propionate, t-nethyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate or ethyl 3-ethoxypropionate.

LEGAL STATUS

[Date of request for examination] 18.11.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of

rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (A) Contain the compound which generates an acid by the exposure of an activity beam of light or a radiation, and the repeat unit which has the radical of (B) following general formula (I-1) – (I-4) expressed with either at least. The resin which disassembles according to an operation of an acid and the solubility over alkali increases, and the solvent which contains the solvent of (C) following (a) 60 to 90% of the weight to all solvents, (a) Propylene-glycol-monomethyl-ether acetate, propylene-glycol-monomethyl-ether propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, the positive type photoresist constituent characterized by containing at least one sort of 1st solvents chosen from 3-ethoxy ethyl propionate.

[Formula 1]

; in general formula (I-1) – (I-4) -- even if R1-R5 are the same, they may differ from each other, and they express the alkyl group, cycloalkyl radical, or alkenyl radical which may have the hydrogen atom and the substituent. Two of R1-R5 may form a ring unitedly.

[Claim 2] The positive type photoresist constituent according to claim 1 characterized by containing the repeat unit which has the alkali fusibility radical protected by at least one sort of radicals of the radicals in which the resin of (B) includes the alicyclic hydrocarbon structure further expressed with following general formula (pI) – (pVI).

[Formula 2]

Inside of general formula (pI) – (pVI); R11 expresses a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, or sec-butyl, and Z expresses an atomic group required to form an alicyclic hydrocarbon radical with a carbon atom. R12-R16 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1-4 carbon numbers, or branching independently respectively, however either at least one, or R15 and R16 express an alicyclic hydrocarbon radical among R12-R14. R17-R21 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of a hydrogen atom

and 1–4 carbon numbers, or branching independently respectively, however at least one of R17–R21 expresses an alicyclic hydrocarbon radical. Moreover, R19 or R21 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1–4 carbon numbers, or branching. R22–R25 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1–4 carbon numbers, or branching independently respectively, however at least one of R22–R25 expresses an alicyclic hydrocarbon radical.

[Claim 3] The positive type photoresist constituent according to claim 2 characterized by a radical including the alicyclic hydrocarbon structure expressed with said general formula (pI) – (pVI) being a radical expressed with the following general formula (II).

[Formula 3]

R28 expresses the alkyl group which may have the substituent among a general formula (II). even if R29–R31 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the hydroxy group, the halogen atom, the carboxy group, or the substituent, an alkenyl radical, an alkoxy group, an alkoxy carbonyl group, or an acyl group. p, q, and r express the integer of 0, or 1–3 independently respectively.

[Claim 4] A positive type photoresist constituent given in either of claims 1–3 characterized by the resin of the above (B) containing the repeat unit expressed with the following general formula (a).

[Formula 4]

R expresses the permutation or the unsubstituted alkyl group of a hydrogen atom, a halogen atom, or carbon numbers 1–4 among a general formula (a). even if R32–R34 are the same, they may differ from each other, and they express a hydrogen atom or a hydroxyl group. At least one of R32–R34 expresses a hydroxyl group.

[Claim 5] Furthermore, the positive type photoresist constituent according to claim 1 to 4 characterized by containing (D) acid diffusion inhibitor.

[Claim 6] The positive type photoresist constituent according to claim 1 to 5 with which the compound of (A) is characterized by being the sulfonate compound of sulfonium or iodonium.

[Claim 7] The positive type photoresist constituent according to claim 1 to 5 with which the compound of (A) is characterized by being the sulfonate compound of N-hydroxy imide, or a disulfo nil diazomethane compound.

[Claim 8] The positive type photoresist constituent according to claim 1 to 7 characterized by using far ultraviolet rays with a wavelength of 150nm – 220nm as an exposure light.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive type photoresist constituent used for super-micro lithography processes, such as a VLSI and manufacture of a high capacity microchip, or other photofabrication processes. Furthermore, it is related with the positive type photoresist constituent which

can form in detail the far-ultraviolet-rays field containing excimer laser light, and the pattern especially made highly minute using light with a wavelength of 250nm or less.

[0002]

[Description of the Prior Art] In recent years, the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a half micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time using the excimer laser light (XeCl, KrF, ArF, etc.) of short wavelength also in far ultraviolet rays is now examined, it will become. A chemistry multiplier system resist is one of those are used for the pattern formation of the lithography in this wavelength field. Generally a chemistry multiplier system resist can be divided roughly into three kinds, the common-name two-component system, a 2.5 component system, and 3 component system. The two-component system has combined the compound (it is henceforth called the photo-oxide generating agent) and binder resin which generate an acid by the photolysis. This binder resin is resin which has in intramolecular the radical (it is also called an acidolysis nature machine) to which an operation of an acid decomposes into and the solubility in the inside of the alkali developer of resin is made to increase. A 2.5 component system contains the low molecular weight compound which has an acidolysis nature machine further in such the two-component system. 3 component system contains a photo-oxide generating agent, alkali fusibility resin, and the above-mentioned low molecular weight compound.

[0003] Although the above-mentioned chemistry multiplier system resist is suitable for ultraviolet rays or the photoresist for an far-ultraviolet-rays exposure, it is necessary to correspond to the demand characteristics on use further in it. Although the resin with which the alicyclic hydrocarbon part was introduced for the purpose of dry etching resistance grant is proposed as a photoresist constituent for the ArF light sources Harder [which becomes very in canal], a system as evil of alicyclic hydrocarbon part installation The development in the tetramethylammonium hydroxide (henceforth, TMAH) water solution conventionally used broadly as a resist developer becomes difficult, or the phenomenon of a resist separating from a substrate in development is seen. Although correspondence of mixing organic solvents, such as isopropyl alcohol, with a developer is considered corresponding to hydrophobing of such a resist and a temporary result is seen, it cannot necessarily be referred to as that the between title was solved that concern and the process of the swelling of the resist film become complicated etc. Many measures of compensating various canal alicyclic hydrocarbon parts with approach called amelioration of a resist by installation of a hydrophilic group are also made.

[0004] The energy susceptibility resist ingredient containing the polymer obtained by carrying out the polymerization of the monomer which has the monomer which has alicyclic structures, such as a norbornene ring, in a principal chain, a maleic anhydride, and a carboxyl group to JP,10-10739,A is indicated. The radiation-sensitive resin constituent containing the resin which has an alicyclic frame in a principal chain, and a radiation-sensitive acid generator is indicated by JP,10-111569,A. Using the resin containing a polar-group content alicyclic functional group and an acidolysis nature machine for radiation sensitive material is indicated by JP,11-109632,A. As for the resin containing the acidolysis nature machine used for the photoresist for far-ultraviolet-rays exposure, it is common to intramolecular to contain the

cyclic-hydrocarbon radical of aliphatic series in coincidence. For this reason, resin became hydrophobicity, and while originating in it, **** existed. although above various means to improve it were examined variously, there are many points still inadequate about the above-mentioned technique about development nature especially, and an improvement is desired.

[0005] That is, also in the technique which makes the above-mentioned far-ultraviolet beam of light and the light source of short wavelength, for example, an ArF excimer laser, (193nm) the exposure light source, there was still room of amelioration in development nature. Specifically, there was a problem of generating of a development defect and generating of edge roughness. Here, since the edge of the crowning of the Rhine pattern of a resist and a pars basilaris ossis occipitalis originates in the property of a resist and is irregularly changed in the direction perpendicular to the direction of Rhine, edge roughness means that an edge is uneven and it is visible, when a pattern is seen from right above. Furthermore, there was room of an improvement also in the problem of a dependency of condensation and rarefaction. Various patterns as an inclination of the latest device, or since it is contained, the resist is asked for various engine performance, and a dependency of condensation and rarefaction is in one of them. That is, as compared with Rhine, a pattern with a large tooth space and also isolated Rhine exist in a device conversely with the part in which Rhine crowds. For this reason, it is important to resolve various Rhine with high repeatability. However, it is not necessarily easy by the optical factor to make various Rhine reproduce, and the present condition is that the solution approach by the resist is not clear in. The engine-performance difference of an isolated pattern and a high density pattern is remarkable in the resist system which contains the above-mentioned alicyclic radical especially, and an improvement is desired.

[0006] Former very generally glycol ether ester like glycol ether, 2-methoxyethanol, and 2-ethoxyethanol and those acetate, for example, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, etc. have been used for the spreading solvent of the positive type photoresist of naphthoquinonediazide / novolak resin system on the other hand conventionally. However, in these solvents, there is a problem in toxicity, the spreading engine performance, the preservation stability of a solution, the resist engine performance, etc., and amelioration was desired. It is known by these spreading engine performance, the preservation stability of a solution, and the list that it is the property of acting greatly with the solvent while it is the attribute which the resist engine performance requires for constituents, such as a binder polymer and a photo-oxide generating agent. However, although it is required for a resist solvent to be satisfied with coincidence of all the requirements for the spreading engine performance, the preservation stability of a solution, safety, the resist engine performance, and a development defect, in the chemistry magnification resist using the polymer which has an alicyclic hydrocarbon frame, the actual condition was hardly known until now.

[0007]

[Problem(s) to be Solved by the Invention] As mentioned above, with the well-known technique of the conventional photoresist constituent, adhesion with sensibility, resolution, and a substrate does not reply to the latest military requirement, and further, since roughness was looked at by generating of a development defect, and the edge of a pattern and a stable pattern was not obtained, the further amelioration was desired. Therefore, the purpose of this invention is solving the technical problem of the improvement technique in the engine performance of above-mentioned micro photofabrication original which uses far-ultraviolet light,

especially ArF excimer laser light, is excellent in sensibility, resolving power, dry etching-proof nature, and adhesion with a substrate, and, specifically, is to offer the positive type photoresist constituent which solved the problem of development defective generating in the case of development, and generating of edge roughness further. The further purpose of this invention is to offer the positive type photoresist constituent for far-ultraviolet-rays exposure excellent in the dependency of condensation and rarefaction.

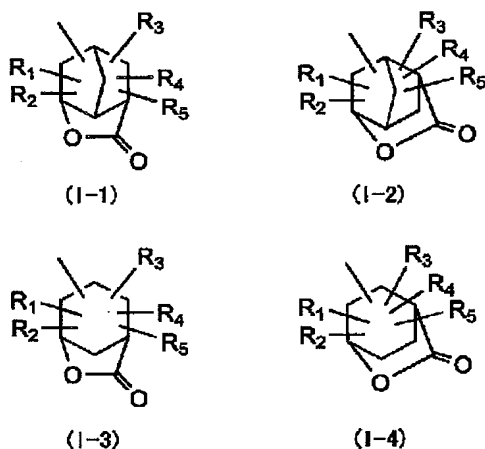
[0008]

[Means for Solving the Problem] As a result of examining wholeheartedly the component of the resist constituent in a positive type chemistry multiplier system, by using specific acidolysis nature resin and a specific solvent, this invention person etc. knew that the purpose of this invention would be attained, and resulted in this invention. That is, the above-mentioned purpose is attained by the following configuration.

[0009] (1) The compound which generates an acid by the exposure of (A) activity beam of light or a radiation, And contain the repeat unit which has the radical of (B) following general formula (I-1) – (I-4) expressed with either at least. The resin which disassembles according to an operation of an acid and the solubility over alkali increases, and the solvent which contains the solvent of (C) following (a) 60 to 90% of the weight to all solvents, (a) Propylene-glycol-monomethyl-ether acetate, propylene-glycol-monomethyl-ether propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, the positive type photoresist constituent characterized by containing at least one sort of 1st solvents chosen from 3-ethoxy ethyl propionate.

[0010]

[Formula 5]

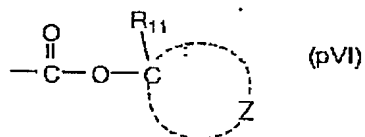
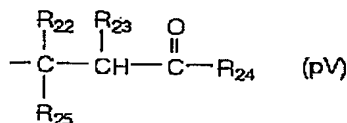
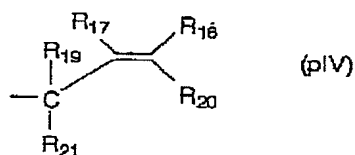
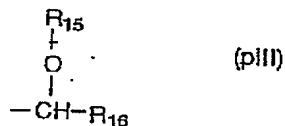
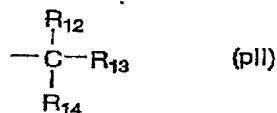


[0011] ; in general formula (I-1) – (I-4) -- even if R1–R5 are the same, they may differ from each other, and they express the alkyl group, cycloalkyl radical, or alkenyl radical which may have the hydrogen atom and the substituent. Two of R1–R5 may form a ring unitedly.

(2) A positive type photoresist constituent given in the above (1) characterized by containing the repeat unit which has the alkali fusibility radical protected by at least one sort of radicals of the radicals in which the resin of (B) includes the alicyclic hydrocarbon structure further expressed with following general formula (pI) – (pVI).

[0012]

[Formula 6]

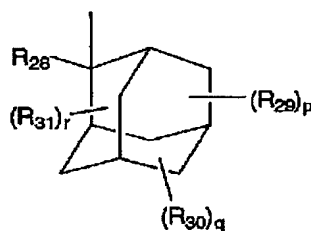


[0013] Inside of general formula (pI) – (pVI); R11 expresses a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, or sec-butyl, and Z expresses an atomic group required to form an alicyclic hydrocarbon radical with a carbon atom. R12–R16 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1–4 carbon numbers, or branching independently respectively, however either at least one, or R15 and R16 express an alicyclic hydrocarbon radical among R12–R14. R17–R21 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of a hydrogen atom and 1–4 carbon numbers, or branching independently respectively, however at least one of R17–R21 expresses an alicyclic hydrocarbon radical. Moreover, R19 or R21 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1–4 carbon numbers, or branching. R22–R25 express the alkyl group or alicyclic hydrocarbon radical of the straight chain of 1–4 carbon numbers, or branching independently respectively, however at least one of R22–R25 expresses an alicyclic hydrocarbon radical.

(3) A positive type photoresist constituent given in the above (2) characterized by a radical including the alicyclic hydrocarbon structure expressed with said general formula (pI) – (pVI) being a radical expressed with the following general formula (II).

[0014]

[Formula 7]



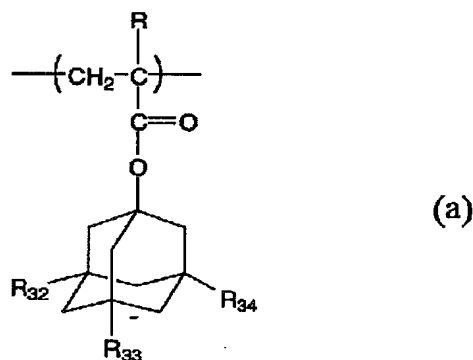
(II)

[0015] R₂₈ expresses the alkyl group which may have the substituent among a general formula (II). even if R₂₉–R₃₁ are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the hydroxy group, the halogen atom, the carboxy group, or the substituent, an alkenyl radical, an alkoxy group, an alkoxy carbonyl group, or an acyl group. p, q, and r express the integer of 0, or 1–3 independently respectively.

(4) A positive type photoresist constituent given in either of the above (1) characterized by the resin of the above (B) containing the repeat unit expressed with the following general formula (a) to (3).

[0016]

[Formula 8]



[0017] R expresses the permutation or the unsubstituted alkyl group of a hydrogen atom, a halogen atom, or carbon numbers 1–4 among a general formula (a). even if R₃₂–R₃₄ are the same, they may differ from each other, and they express a hydrogen atom or a hydroxyl group. At least one of R₃₂–R₃₄ expresses a hydroxyl group.

(5) A positive type photoresist constituent given in either of aforementioned (1) – (4) characterized by furthermore containing (D) acid diffusion inhibitor.

(6) A positive type photoresist constituent given in either of aforementioned (1) – (5) to which the compound of (A) is characterized by being the sulfonate compound of sulfonium or iodonium.

(7) A positive type photoresist constituent given in either of aforementioned (1) – (5) to which the compound of (A) is characterized by being the sulfonate compound of N-hydroxy imide, or a disulfo nil diazomethane compound.

(8) A positive type photoresist constituent given in either of aforementioned (1) – (7) characterized by using far ultraviolet rays with a wavelength of 150nm – 220nm as an exposure light.

[0018]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained in detail. The (A) photo-oxide generating agent used by <compound [which generates an acid by the exposure of (A) activity beam of light or a radiation] (photo-oxide generating agent)> this invention is a compound which generates an acid by the exposure of an activity beam of light or a radiation. As a photo-oxide generating agent used by this invention, the photoinitiator of optical cationic polymerization, a well-known light (400–200nm ultraviolet rays and far ultraviolet rays — preferably especially) currently used for the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist The compounds which generate an acid by g line, h line, i line, KrF excimer laser light, ArF excimer laser light, the electron ray, the X-ray, the molecular beam, or the ion beam, and those mixture can be used choosing them suitably. Moreover, the compound which is represented by onium salt, such as diazonium salt, ammonium salt, phosphonium salt, iodonium salt, sulfonium salt, a seleno NIUMU salt, and arsonium salt, an organic halogenated compound, an organic metal / organic halogenide, the photo-oxide generating agent that has o-nitrobenzyl mold protective group, imino sulfonate, etc. as a photo-oxide generating agent used for other this inventions, for example and which photodissociates and generates a sulfonic acid, a disulfon compound, a diazo keto sulfone, a diazo disulfon compound, etc. can be mentioned. Moreover, the radical which generates an acid by such light, or the compound which introduced the compound into the principal chain or side chain of a polymer can be used.

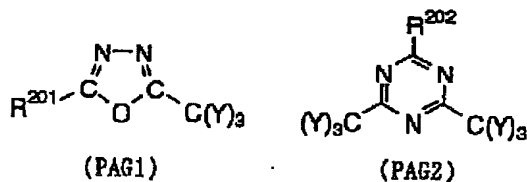
[0019] Furthermore, the compound which generates an acid by the light of a publication can also be used for V.N.R.Pillai, Synthesis, (1), 1 (1980), A.Abadetal, TetrahedronLett., (47) 4555 (1971), D.H.R.Bartonetal, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0020] In the compound which decomposes by the exposure of the above-mentioned activity beam of light or a radiation, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0021]

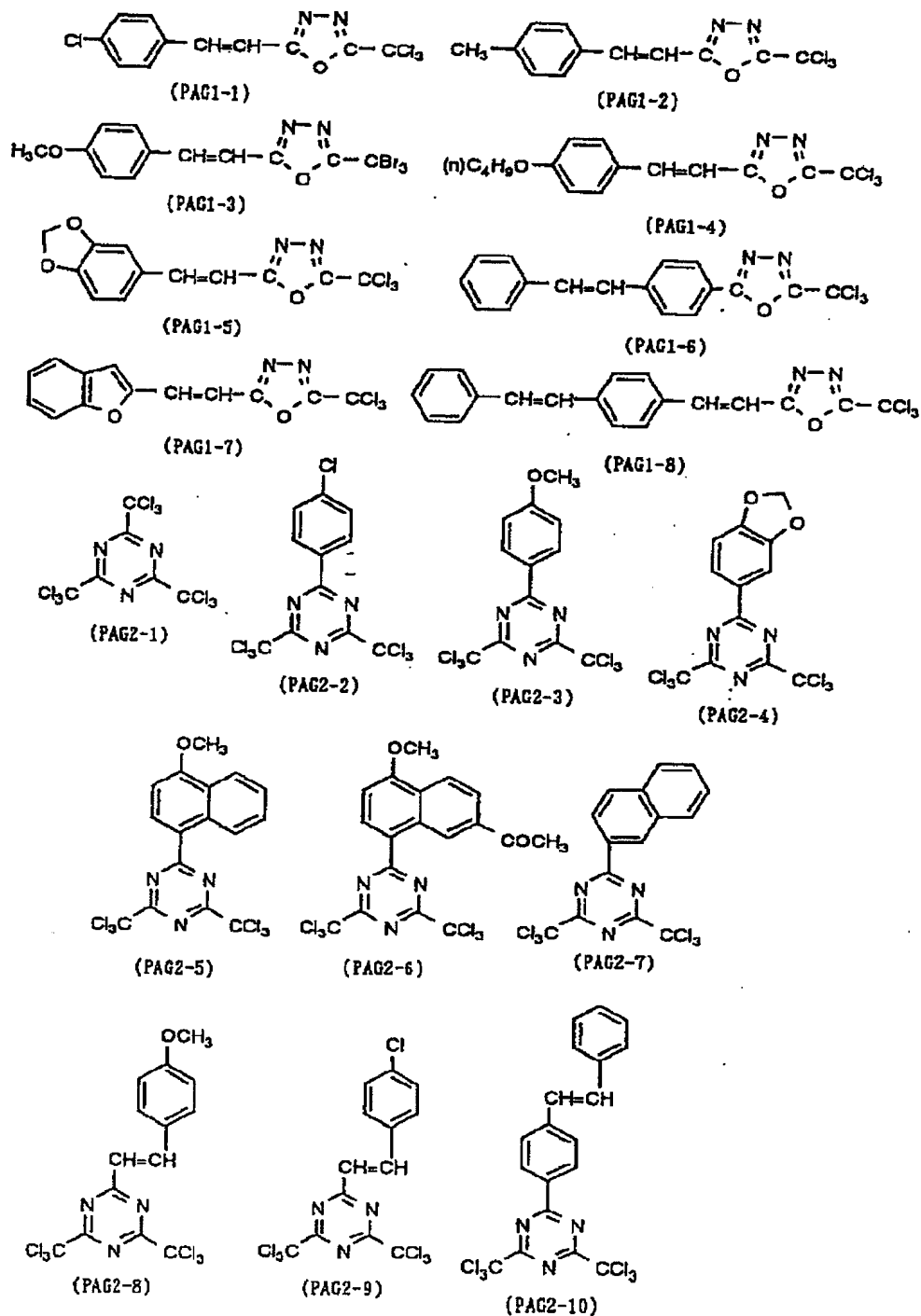
[Formula 9]



[0022] R201 shows among a formula the aryl group which is not permuted [a permutation or] and an alkenyl radical, and R202 shows the aryl group which is not permuted [a permutation or], an alkenyl radical, an alkyl group, and –C (Y)3. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

[0023]

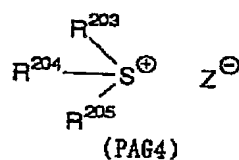
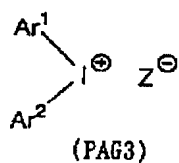
[Formula 10]



[0024] (2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0025]

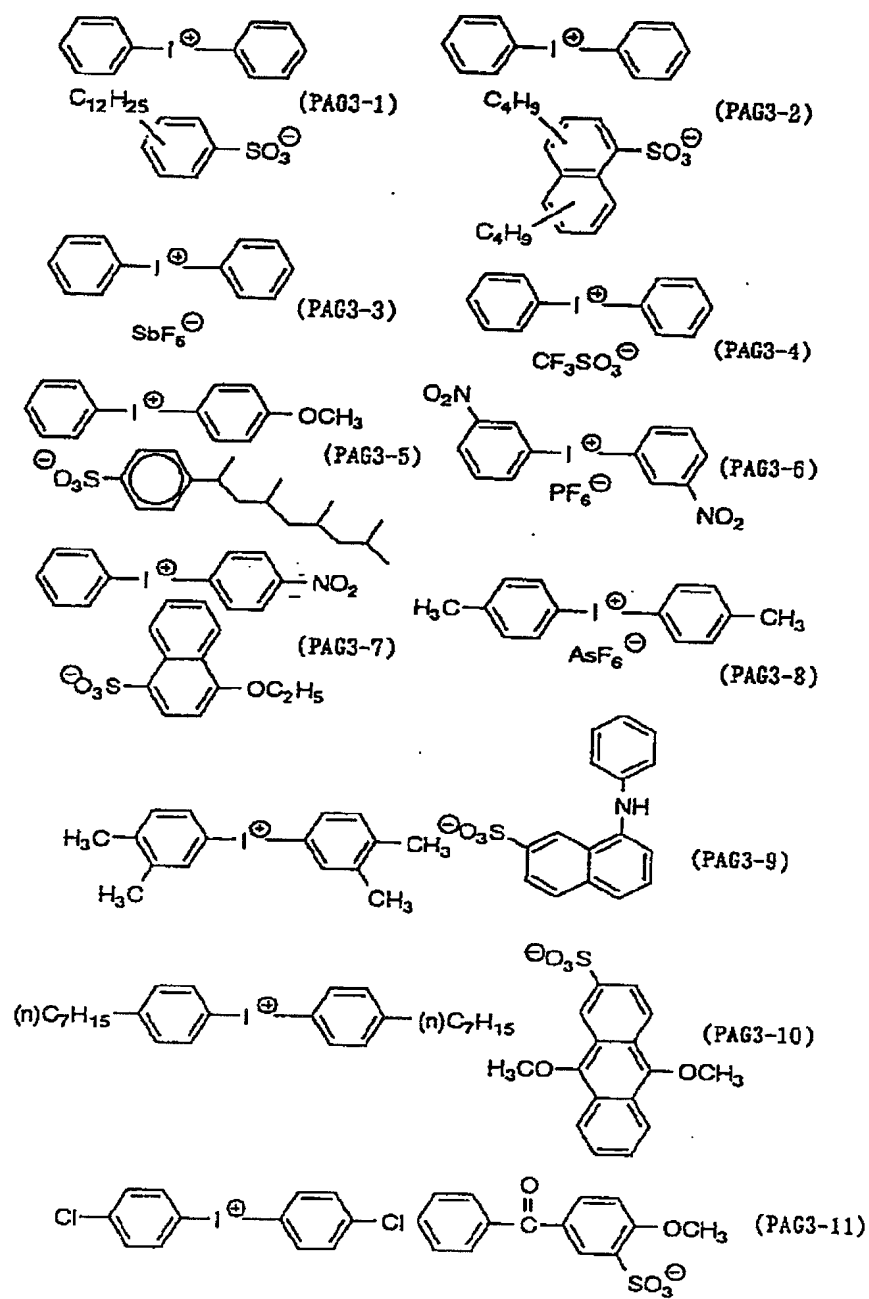
[Formula 11]



[0026] Formulas Ar1 and Ar 2 show respectively the aryl group which is not permuted [a permutation or] independently here. R203, R204, and R205 show respectively the alkyl group which is not permuted [a permutation or] and an aryl group independently. Although Z- can show an opposite anion, for example, can mention condensation polykaryotic aromatic series sulfonic-acid anions, such as permutation benzenesulfonic acid anions, such as perfluoro alkane sulfonic-acid anions, such as BF_4^- , AsF_6^- , PF_6^- , SbF_6^- , SiF_6^{2-} , ClO_4^- , and CF_3SO_3^- , a toluenesulfonic acid anion, the dodecylbenzenesulfonic acid anion, and a pentafluoro benzenesulfonic acid anion, a naphthalene-1-sulfonic-acid anion, and an anthraquinone sulfonic-acid anion, a sulfonic group content color, etc., it is not limited to these. Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent. Although the compound shown below as an example is mentioned, it is not limited to these.

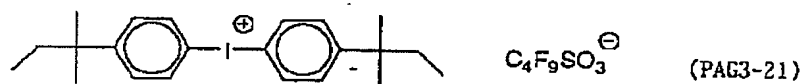
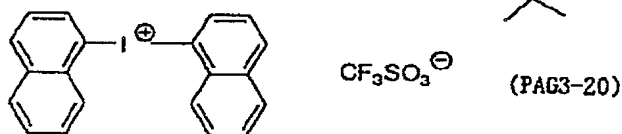
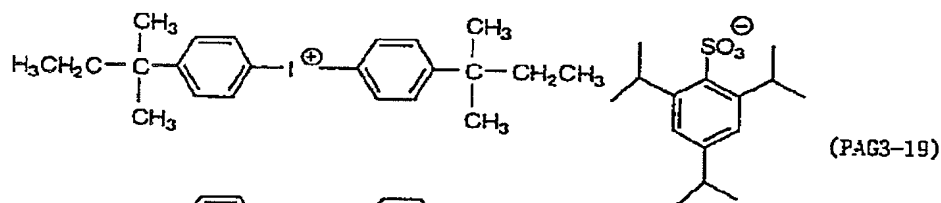
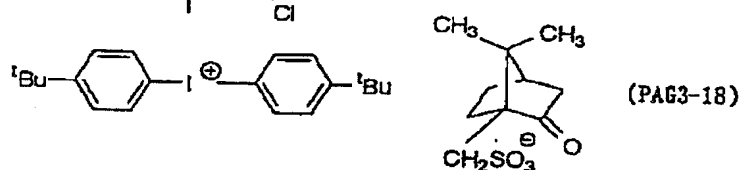
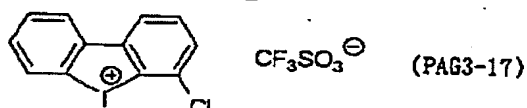
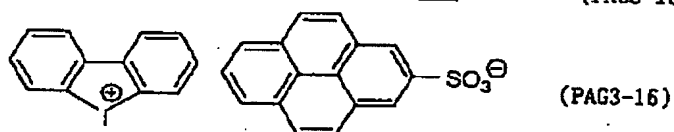
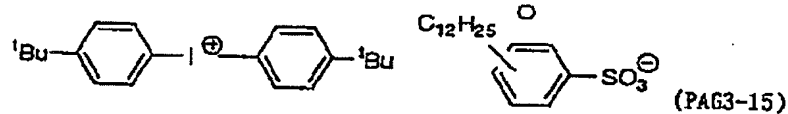
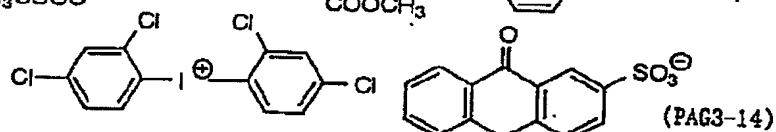
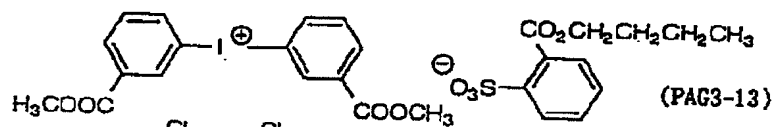
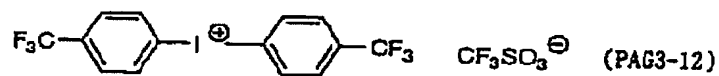
[0027]

[Formula 12]



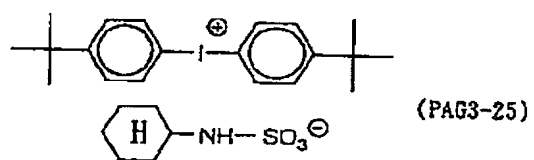
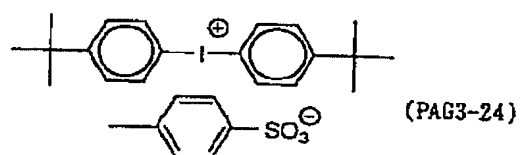
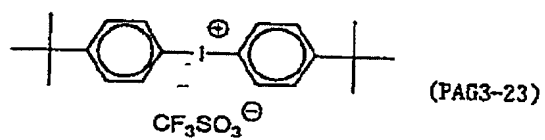
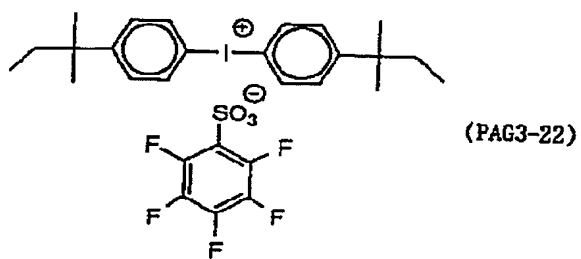
[0028]

[Formula 13]



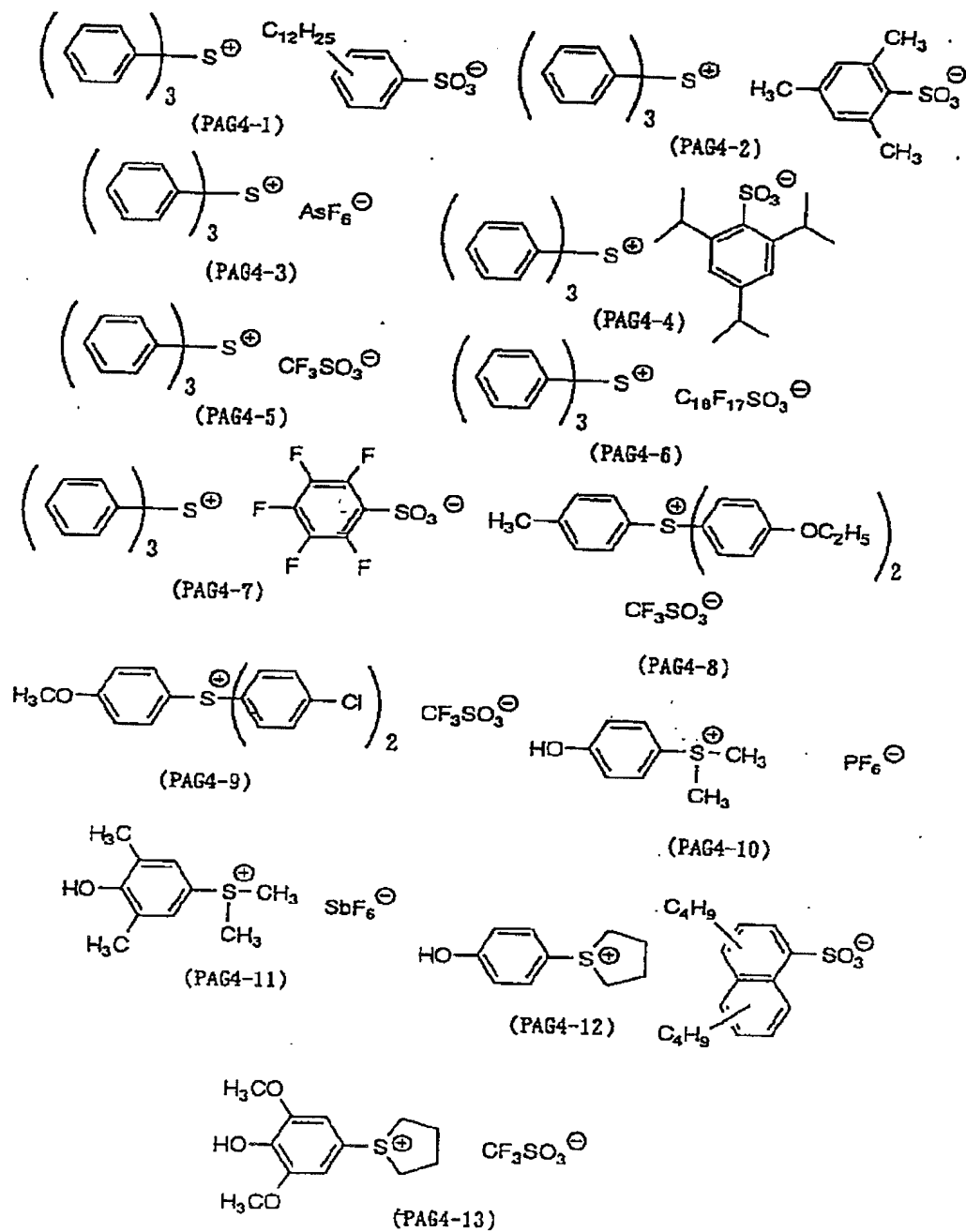
[0029]

[Formula 14]



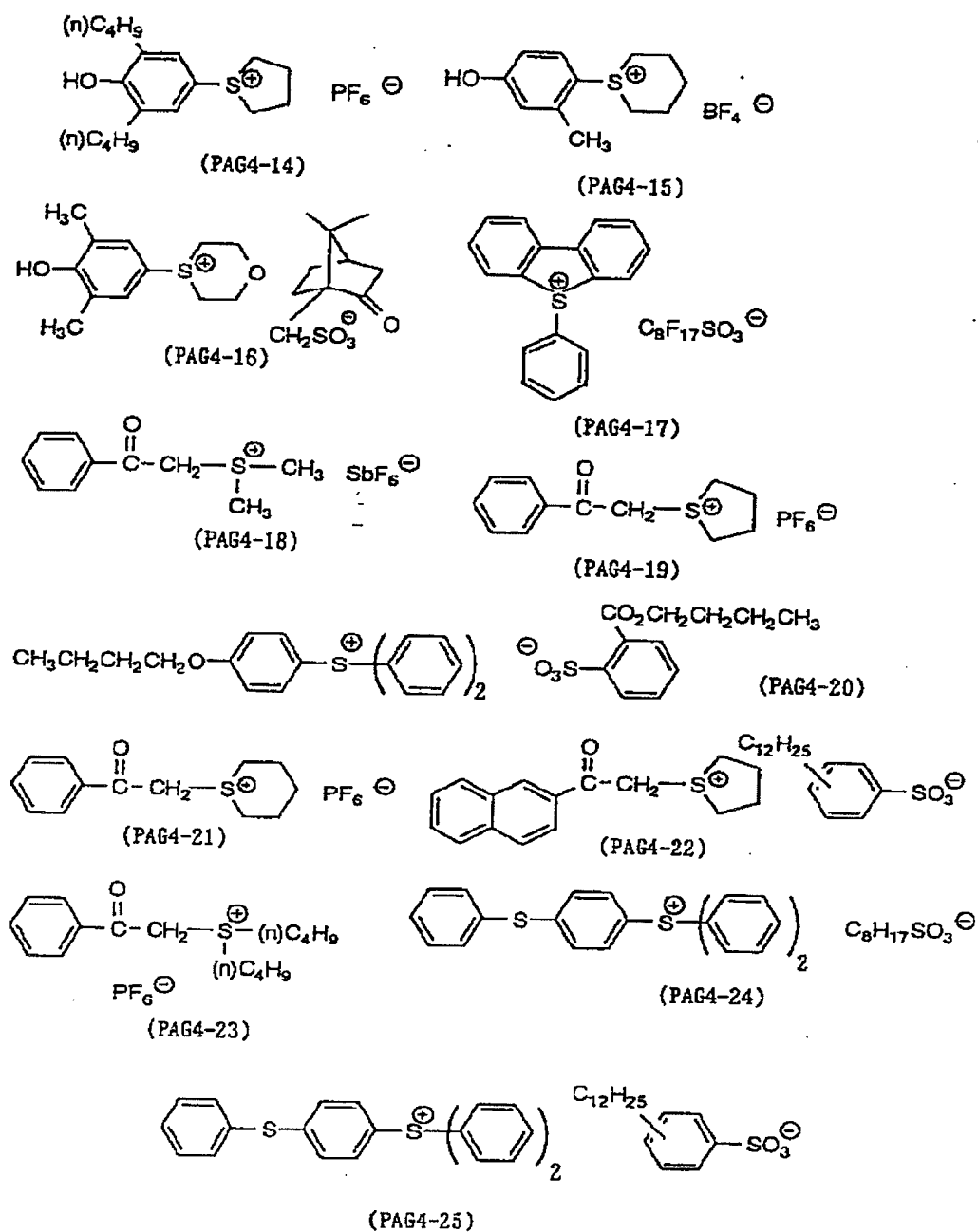
[0030]

[Formula 15]



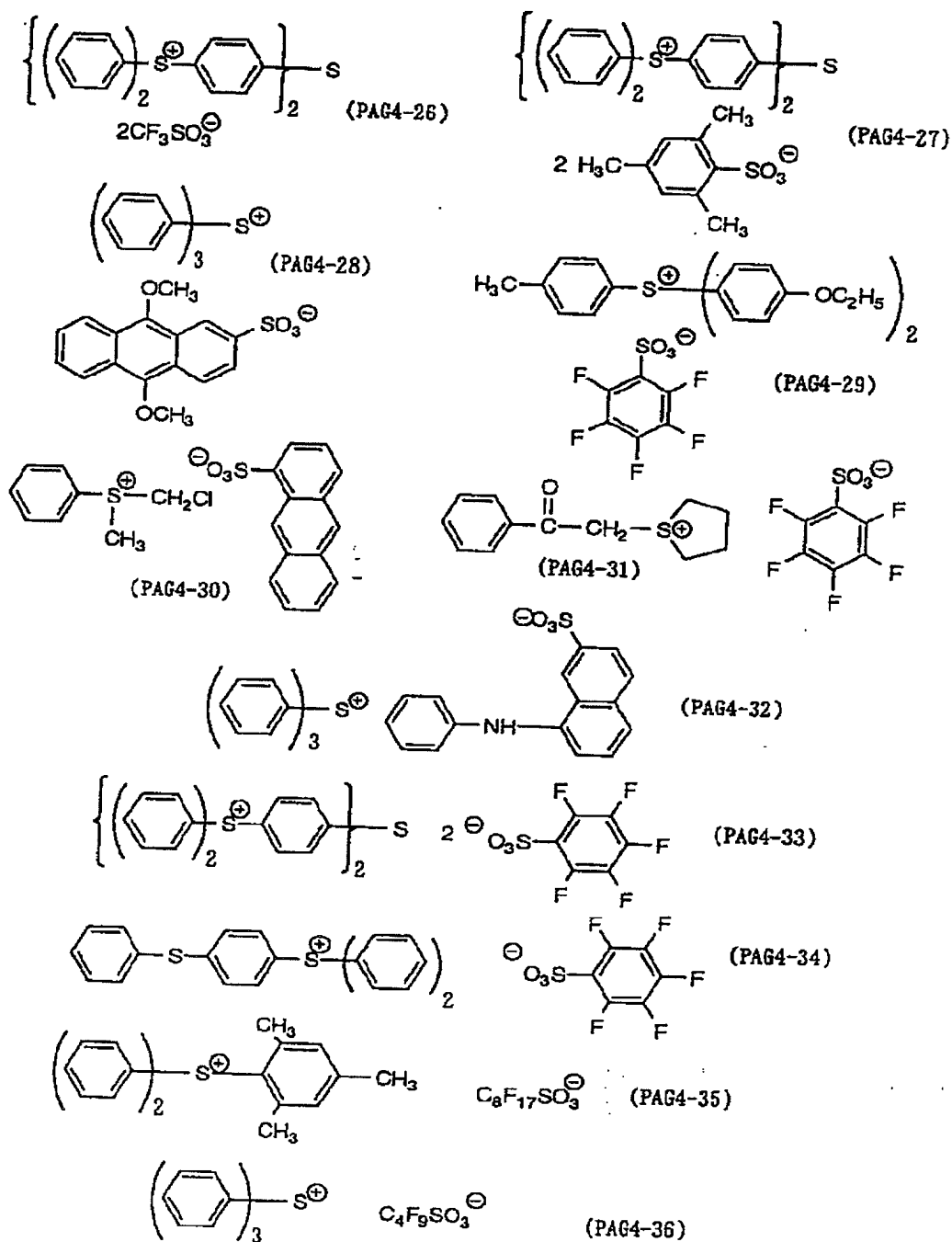
[0031]

[Formula 16]



[0032]

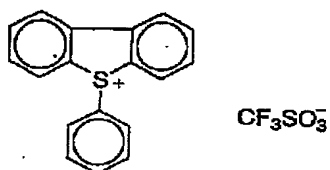
[Formula 17]



[0033]

[Formula 18]

PAG4-37



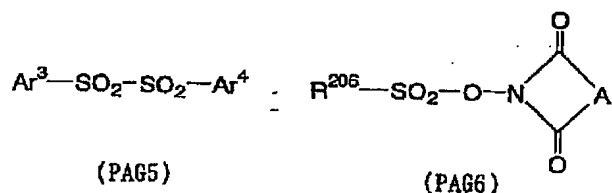
[0034] The above-mentioned onium salt shown by the general formula (PAG3) and (PAG4) is well-known.

For example, J.W.Knapczyketal, J.Am.Chem.Soc., 91,145 (1969), A. (L.Maycoketal, J.Org.Chem., 35 and 2532, 1970), E. (Goethasetal, Bull.Soc.Chem.Belg., 73 and 546, 1964), H. 51 M.Leicester, J.Ame.Chem.Soc., 3587 (1929), J. V.Crivelloet It is compoundable by the approach of a publication to al, J.Polym.Chem.Ed., 18 and 2677 (1980), U.S. Pat. No. 2,807,648 and said 4,247,473 numbers, JP,53-101,331,A, etc.

[0035] (3) The imide sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0036]

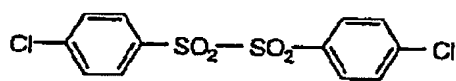
[Formula 19]



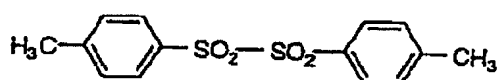
[0037] Ar3 and Ar4 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R206 shows the alkyl group which is not permuted [a permutation or] and an aryl group. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

[0038]

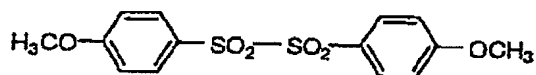
[Formula 20]



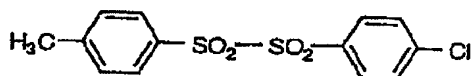
(PAG5-1)



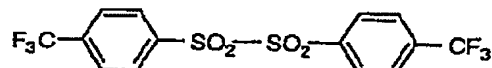
(PAG5-2)



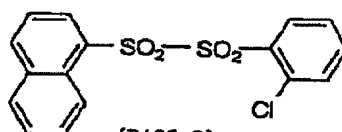
(PAG5-3)



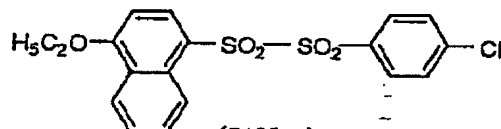
(PAG5-4)



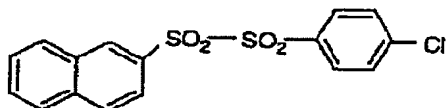
(PAG5-5)



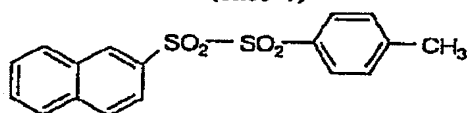
(PAG5-6)



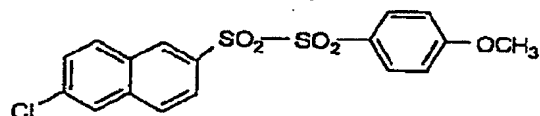
(PAG5-7)



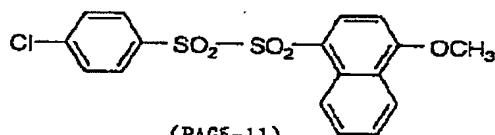
(PAG5-8)



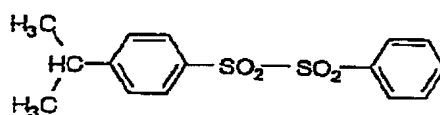
(PAG5-9)



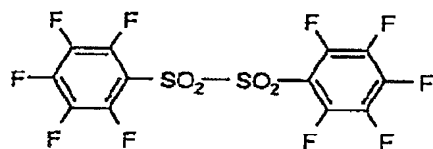
(PAG5-10)



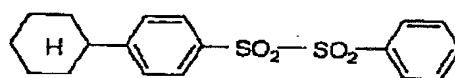
(PAG5-11)



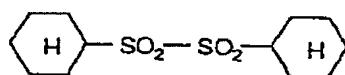
(PAG5-12)



(PAG5-13)



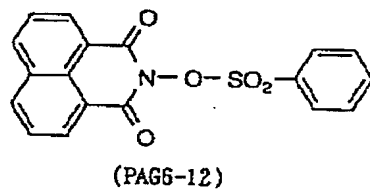
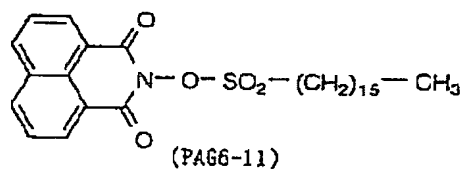
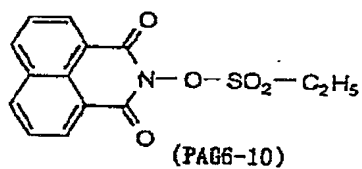
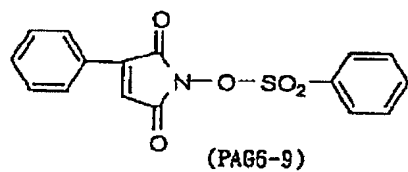
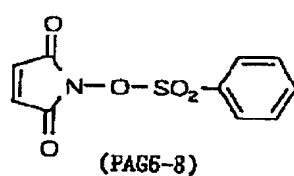
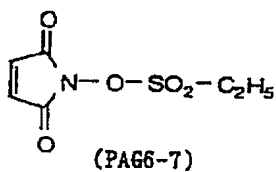
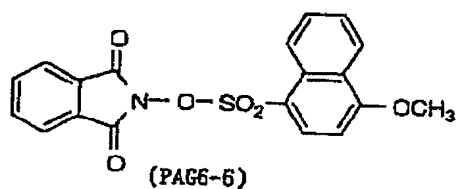
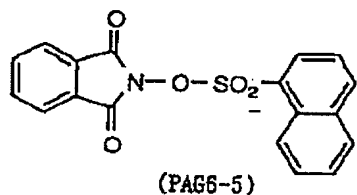
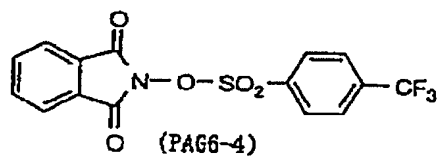
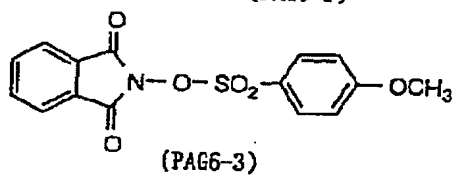
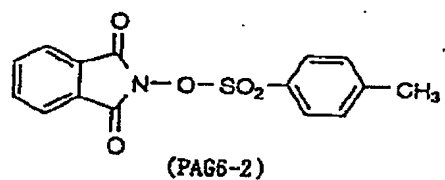
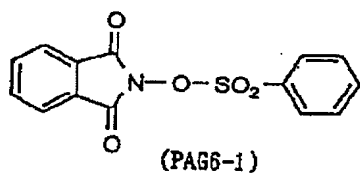
(PAG5-14)



(PAG5-15)

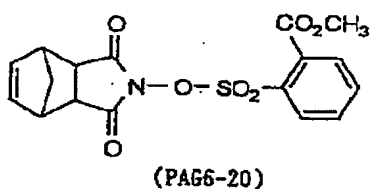
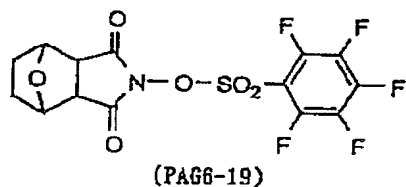
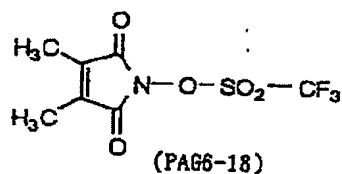
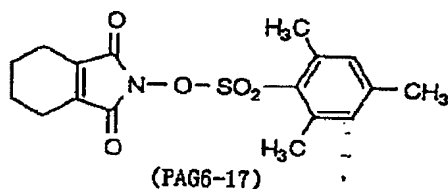
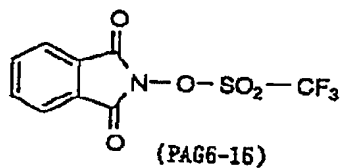
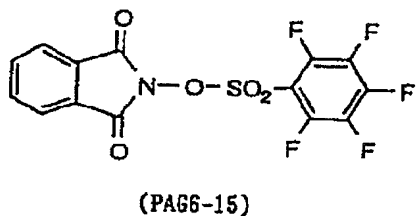
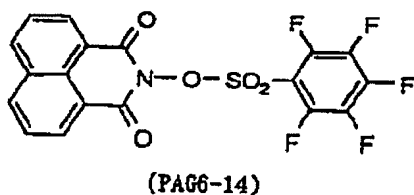
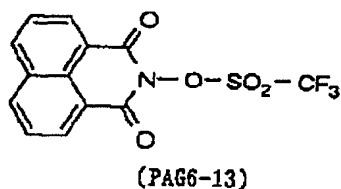
[0039]

[Formula 21]



[0040]

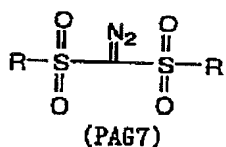
[Formula 22]



[0041] (4) The diazo disulfon derivative expressed with the following general formula (PAG7).

[0042]

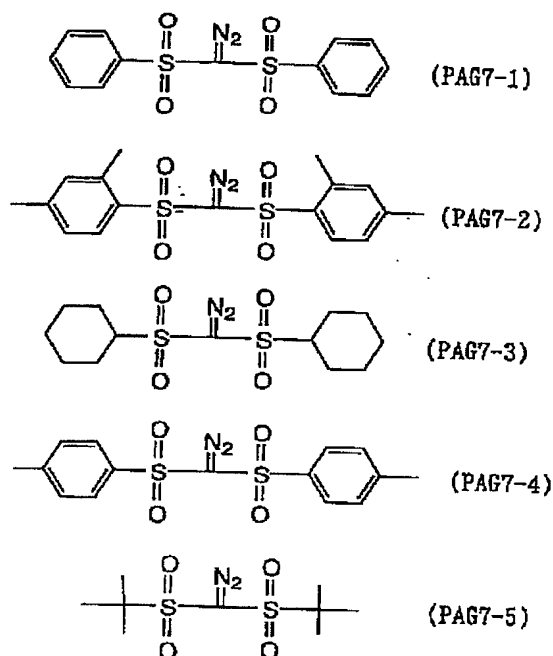
[Formula 23]



[0043] R expresses a straight chain, branching, an annular alkyl group, or the aryl group that may be permuted here. Although the compound shown below as an example is mentioned, it is not limited to these.

[0044]

[Formula 24]



[0045] In this invention, it is desirable as a photo-oxide generating agent that they are the sulfonate compound (compound expressed especially preferably (PAG3) (PAG4)) of sulfonium or iodonium, the sulfonate compound (especially it is desirable (PAG6) compound expressed) of N-hydroxy imide, or a disulfonyl diazomethane compound (especially it is desirable (PAG7) compound expressed). Thereby, sensibility and resolving power are excellent and the edge roughness of a still more detailed pattern comes to be excellent. The addition of these photo-oxide generating agents is usually used in 0.001 – 40% of the weight of the range on the basis of the solid content in a constituent, and is preferably used in 0.1 – 5% of the weight of the range still more preferably 0.01 to 20% of the weight. It becomes [if there are few additions of a photo-oxide generating agent than 0.001 % of the weight, sensibility will become low, and if there are more additions than 40 % of the weight, the light absorption of a resist will become high too much, and / aggravation of a profile and a process (especially BEKU) margin] narrow and is not desirable.

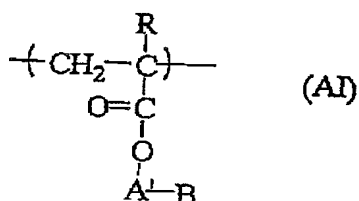
[0046] The resin (only henceforth "the resin of (B)") which disassembles according to an operation of the above-mentioned (B) acid used for the constituent of <(B) Resin which disassembles according to operation of acid and solubility over alkali increases> this invention, and the solubility over alkali increases includes the repeat unit which has the radical expressed with the above-mentioned general formula (I-1) (I-4). In general formula (I-1) – (I-4), as an alkyl group in R1–R5, the alkyl group of the shape of a straight chain and the letter of branching is mentioned, and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the shape of a straight chain of 1–12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1–10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, a decyl group still more preferably As a cycloalkyl radical in R1–R5, the thing of 3–8 carbon numbers, such as a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, and a cyclo octyl radical, is desirable. As an alkenyl radical in R1–R5, the thing of 2–6 carbon

numbers, such as a vinyl group, a propenyl radical, a butenyl group, and a hexenyl radical, is desirable. Moreover, as a ring which two of R1-R5 combine and form, three to 8 membered-rings, such as a cyclopropane ring, a cyclobutane ring, a cyclopentane ring, a cyclohexane ring, and a cyclooctane ring, are mentioned. In addition, R1-R5 may be connected with any of the seven carbon atoms which constitute the annular frame by the general formula (I-1) and (I-2).

[0047] Moreover, as further substituent of the above-mentioned alkyl group, a cycloalkyl radical, and an alkenyl radical, the alkoxy group of 1-4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom), an acyl group, an acyloxy radical, a cyano group, a hydroxyl group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. can be mentioned. As what that has the radical expressed with general formula (I-1) - (I-4) and is desirable as a repeat unit, the repeat unit expressed with the following general formula (AI) is mentioned.

[0048]

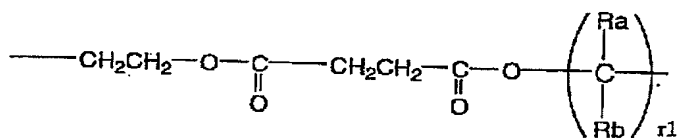
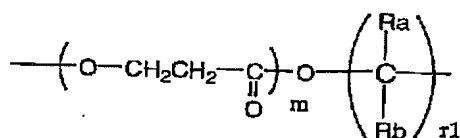
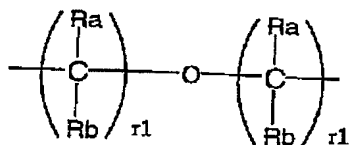
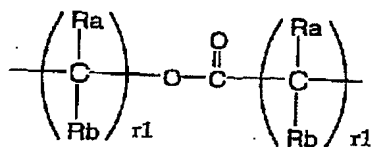
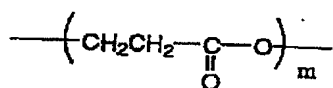
[Formula 25]



[0049] R is synonymous with R in the below-mentioned general formula (a) among a general formula (AI). A' expresses single bond, a ether group, an ester group, a carbonyl group, an alkylene group, or the divalent radical that combined these. B expresses the radical shown by either the general formula (I-1) - (I-4) inside. In A', the thing of the following type is mentioned as a this ***** divalent radical, for example.

[0050]

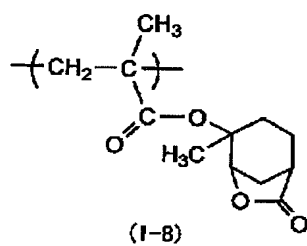
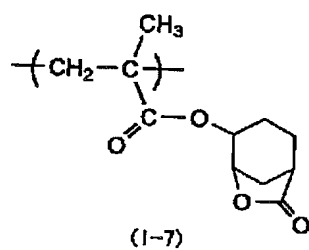
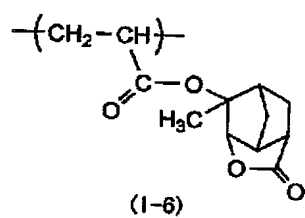
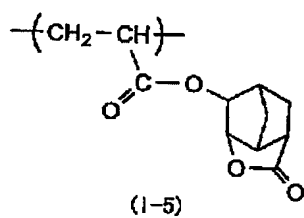
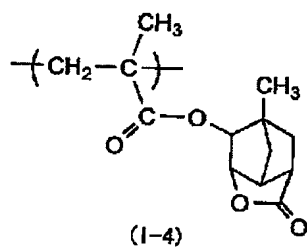
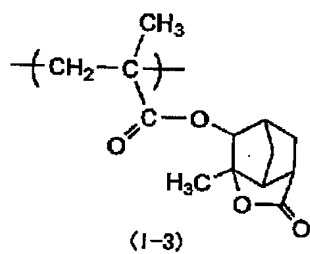
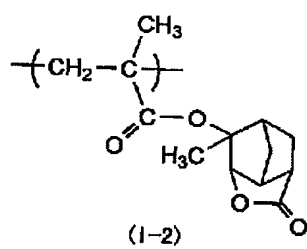
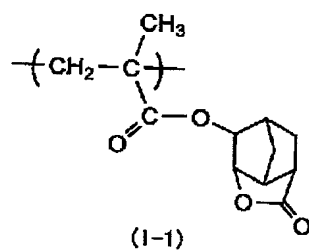
[Formula 26]



[0051] In the above-mentioned formula, Ra, Rb, and r1 are respectively synonymous with the below-mentioned thing. m expresses the integer of 1-3. Although the example of the repeat unit expressed with a general formula (AI) below is given, the contents of this invention are not limited to these.

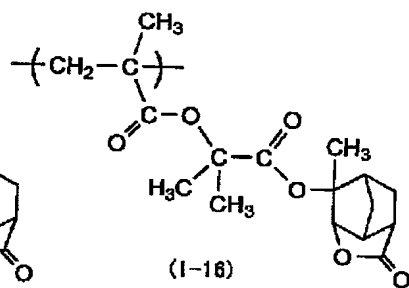
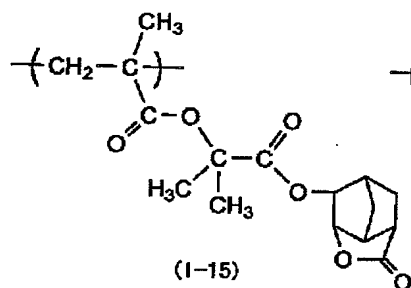
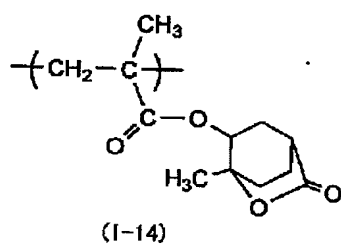
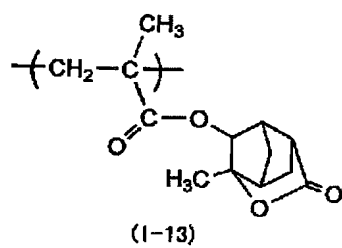
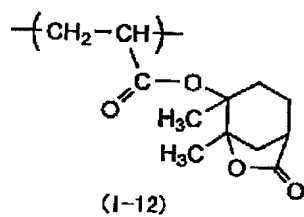
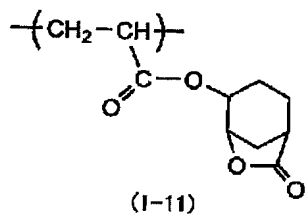
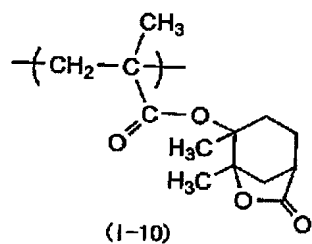
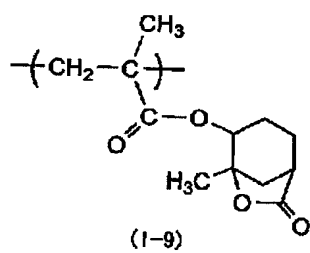
[0052]

[Formula 27]



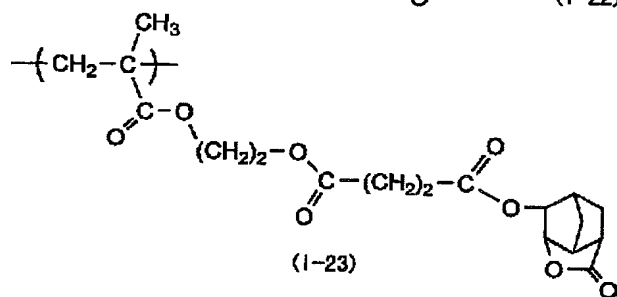
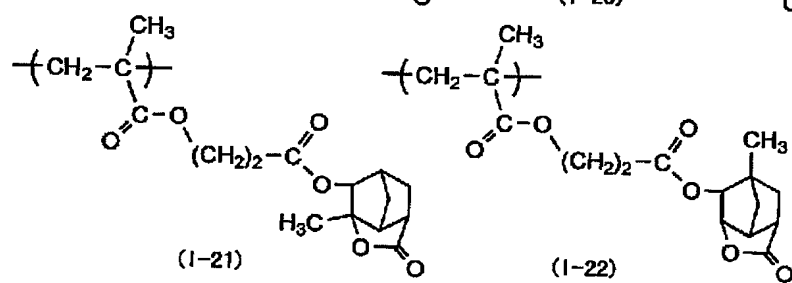
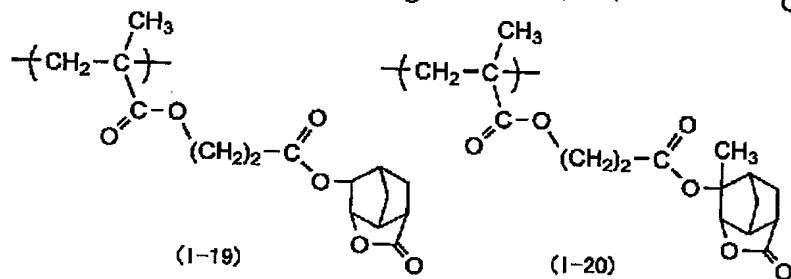
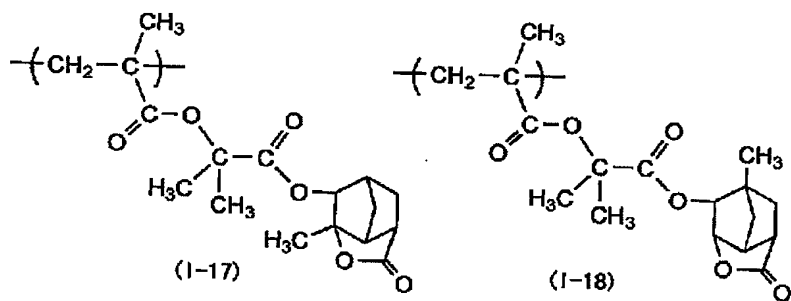
[0053]

[Formula 28]



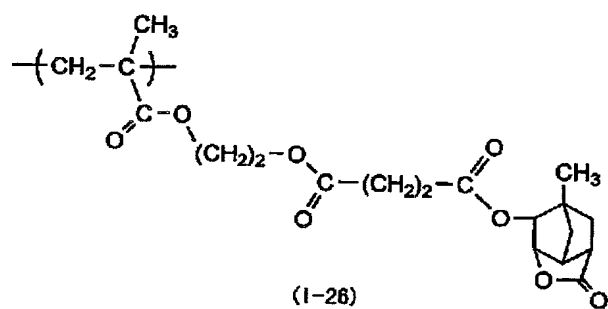
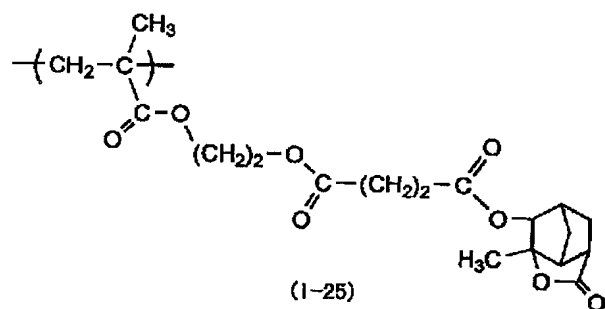
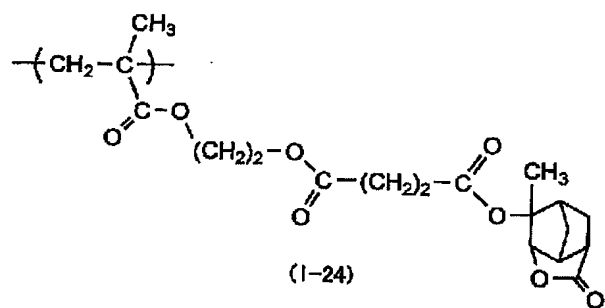
[0054]

[Formula 29]



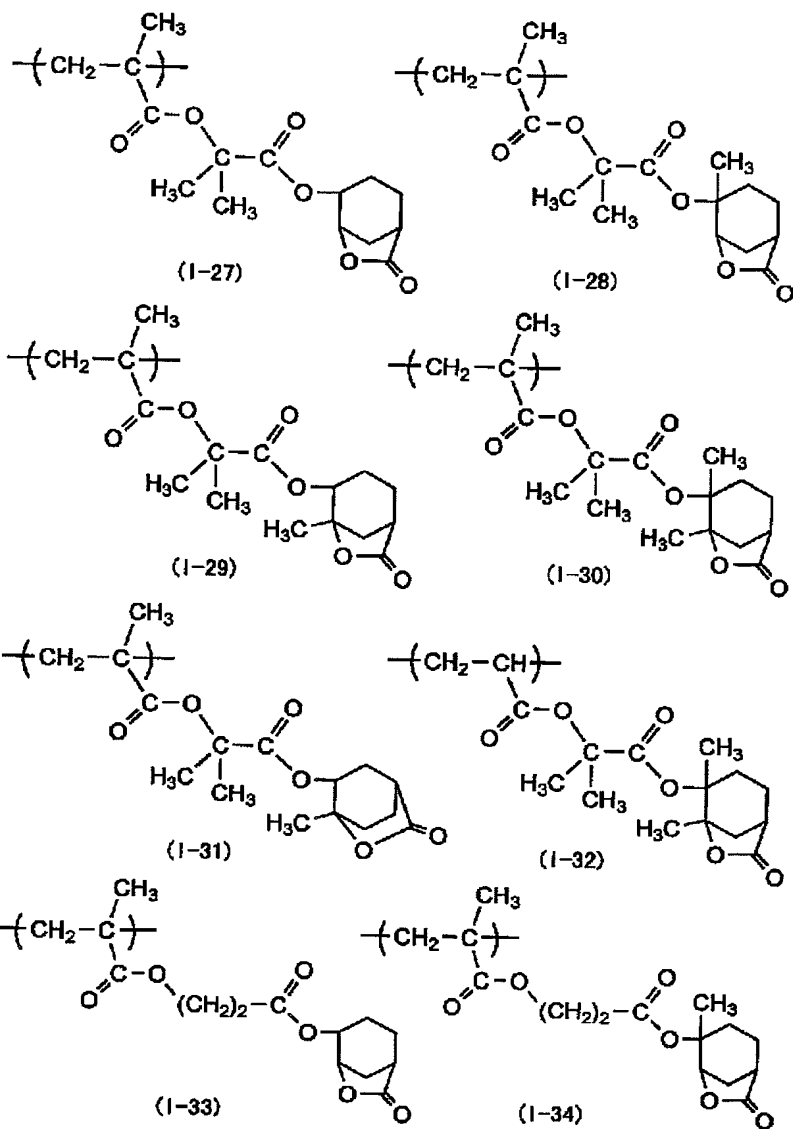
[0055]

[Formula 30]



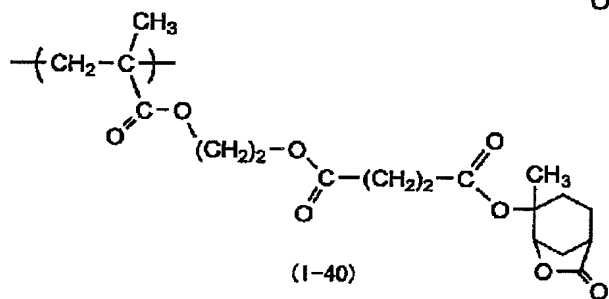
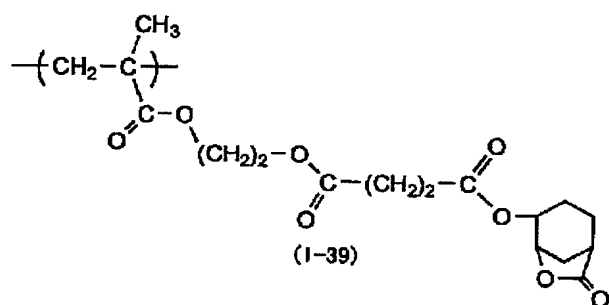
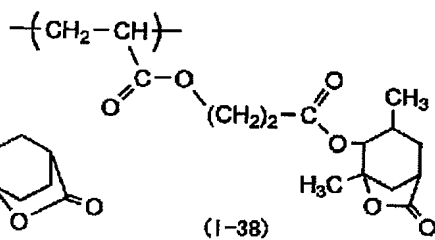
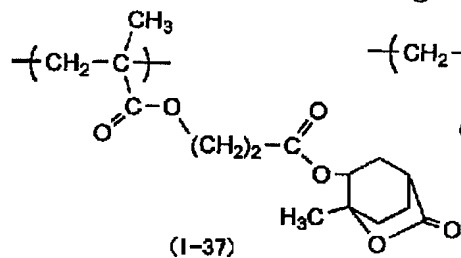
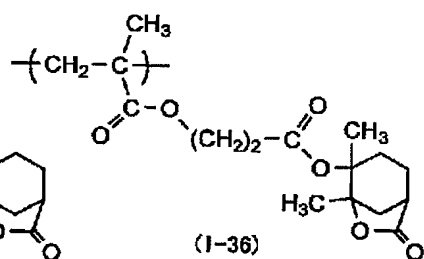
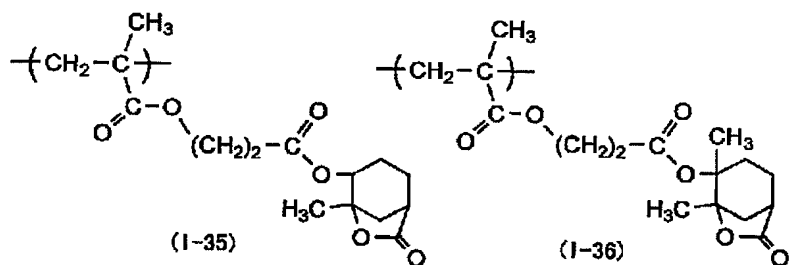
[0056]

[Formula 31]



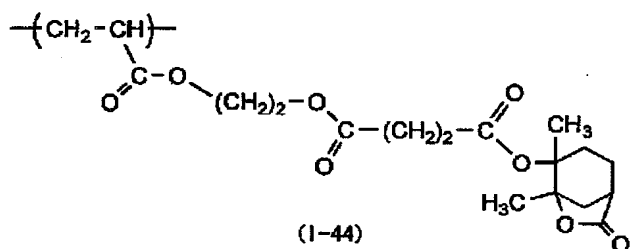
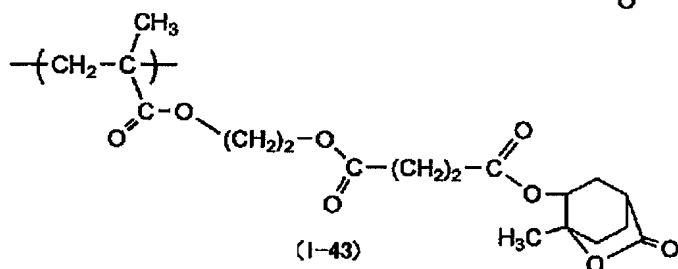
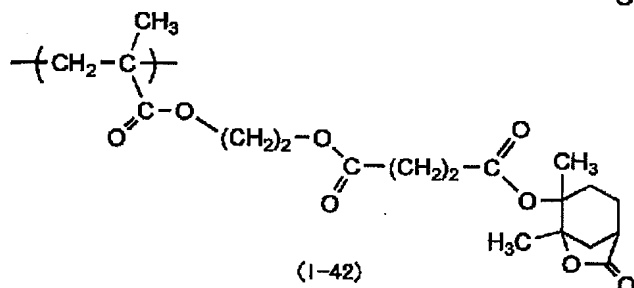
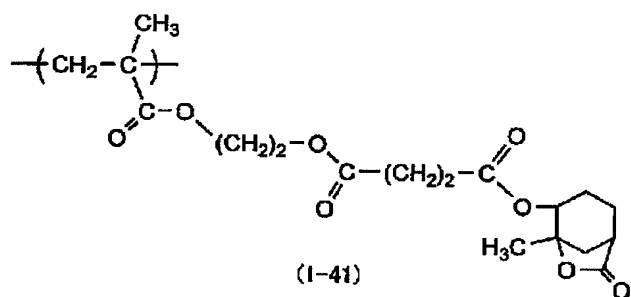
[0057]

[Formula 32]



[0058]

[Formula 33]

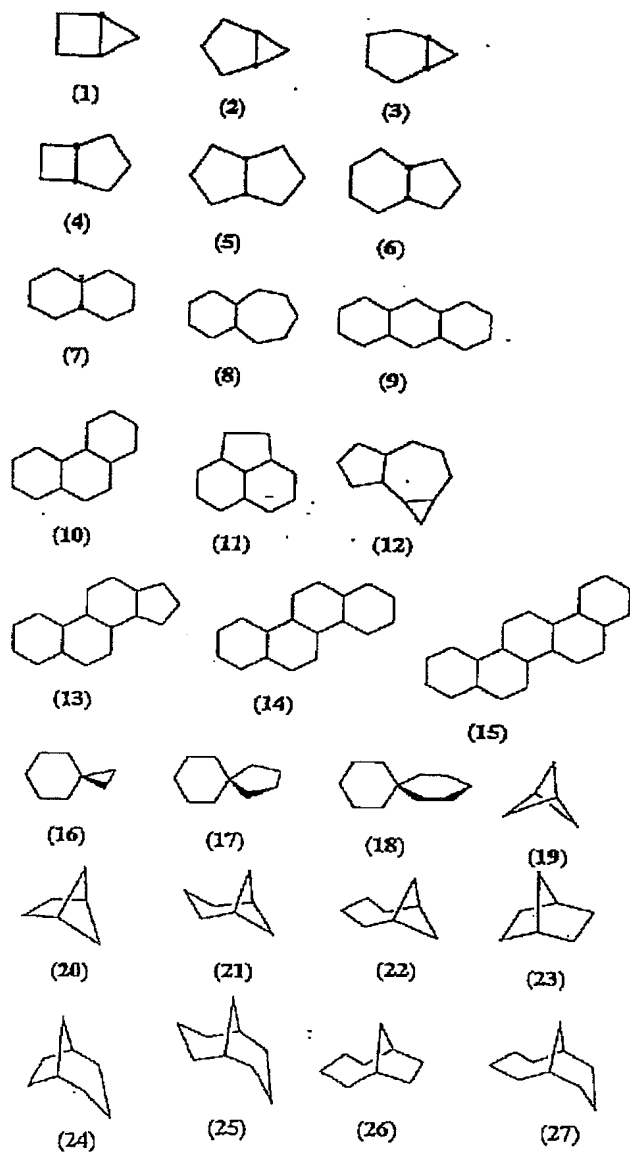


[0059] In this invention, it is desirable to contain the repeat unit which has the alkali fusibility radical protected by at least one sort of radicals of the radicals in which the resin of (B) includes the alicyclic hydrocarbon structure further expressed with above-mentioned general formula (pI) – (pVI) at the point which becomes more remarkable about the effectiveness of this invention. In general formula (pI) – (pVI), the straight chain which has 1–4 carbon atoms which may be a permutation or unsubstituted any as an alkyl group in R12–R25, or the alkyl group of branching is expressed. As the alkyl group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, etc. are mentioned, for example. Moreover, as further substituent of the above-mentioned alkyl group, the alkoxy group of 1–4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom), an acyl group, an acyloxy radical, a cyano group, a hydroxyl group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. can be mentioned. As an alicyclic hydrocarbon radical which the alicyclic hydrocarbon radical, or Z and the carbon atom in R11–R25 form, a monocycle type or a polycyclic type is sufficient. Specifically, the radical which has with a carbon numbers of five or more mono-cyclo, bicyclo one, tricyclo one, tetracyclo structure, etc. can be mentioned. The carbon number has 6–30 desirable pieces, and especially its 7–25

carbon numbers are desirable. These alicyclic hydrocarbon radicals may have the substituent. The example of structure of an alicyclic part is shown among the radicals which include alicyclic hydrocarbon structure in below.

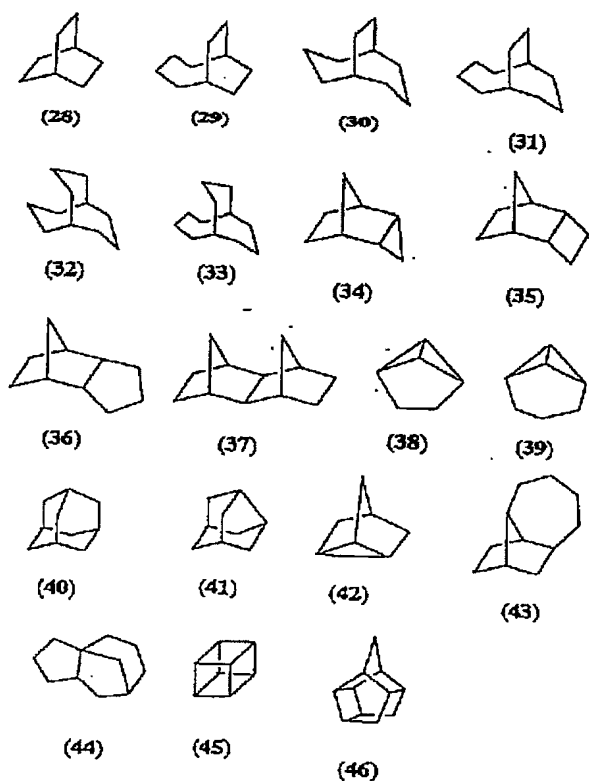
[0060]

[Formula 34]



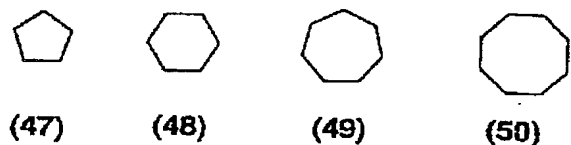
[0061]

[Formula 35]



[0062]

[Formula 36]



[0063] In this invention, an adamantanyl radical, a NORUADA man chill radical, decalin residue, a tricyclo deca nil radical, a tetracyclo dodecanyl radical, a norbornyl radical, a cedrol radical, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclo deca nil radical, and a cyclo dodecanyl radical can be mentioned as what has the above-mentioned desirable alicyclic part. They are an adamantanyl radical, decalin residue, a norbornyl radical, a cedrol radical, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclo deca nil radical, and a cyclo dodecanyl radical more preferably.

[0064] As a substituent of these alicyclic hydrocarbon radicals, an alkyl group, a permutation alkyl group, a cycloalkyl radical, an alkenyl radical, an acyl group, a halogen atom, a hydroxyl group, an alkoxy group, a carboxyl group, and an alkoxy carbonyl group are mentioned. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group (the alkoxy group of an alkoxy carbonyl group is also included), the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a

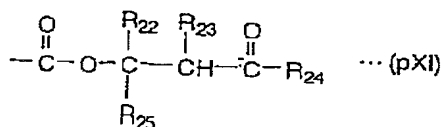
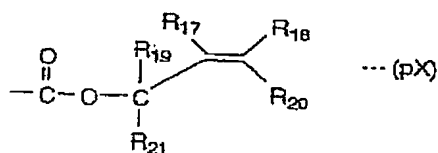
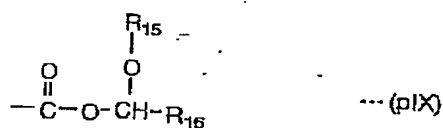
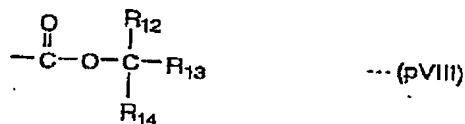
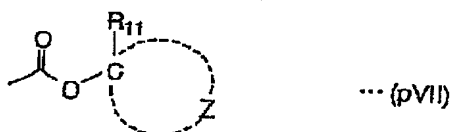
cycloalkyl radical, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, etc. are mentioned. As an alkenyl radical, the alkenyl radical of 2–6 carbon numbers is mentioned, and a vinyl group, a propenyl radical, an allyl group, a butenyl group, a pentenyl radical, a hexenyl radical, etc. are specifically mentioned. As an acyl group, an acetyl group, an ethyl carbonyl group, a propylcarbonyl radical, etc. are mentioned. As a halogen atom, a chlorine atom, a bromine atom, iodine atom, a fluorine atom, etc. are mentioned.

[0065] Also in the structure shown by general formula (pI) – (pVI), it is a general formula (pI) preferably, and is the radical more preferably shown by the above-mentioned general formula (II). The example which mentioned the alkyl group of R28 in a general formula (II), the halogen atom in R29–R31, an alkyl group, a cycloalkyl radical, the alkenyl radical, the alkoxy group, the alkoxy carbonyl group, and the acyl group by the substituent of said alicyclic hydrocarbon radical is given.

[0066] As an alkali fusibility radical protected with the structure shown by general formula (pI) in the above-mentioned resin – (pVI), well-known various radicals are mentioned in this technical field. A carboxylic-acid radical, a sulfonic group, a phenolic group, a thiol group, etc. are mentioned, and, specifically, they are a carboxylic-acid radical and a sulfonic group preferably. The radical preferably expressed with following general formula (pVII) – (pXI) as an alkali fusibility radical protected with the structure shown by general formula (pI) in the above-mentioned resin – (pVI) is mentioned.

[0067]

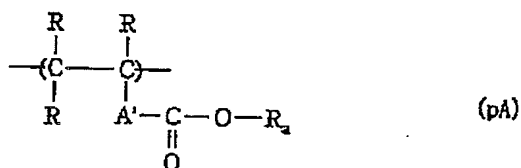
[Formula 37]



[0068] Here, R₁₁-R₂₅, and Z are the same as said definition respectively. As a repeat unit which has the alkali fusibility radical which constitutes the above-mentioned resin, and which was protected with the structure shown by general formula (pI) - (pVI), the repeat unit shown by the following general formula (pA) is desirable.

[0069]

[Formula 38]

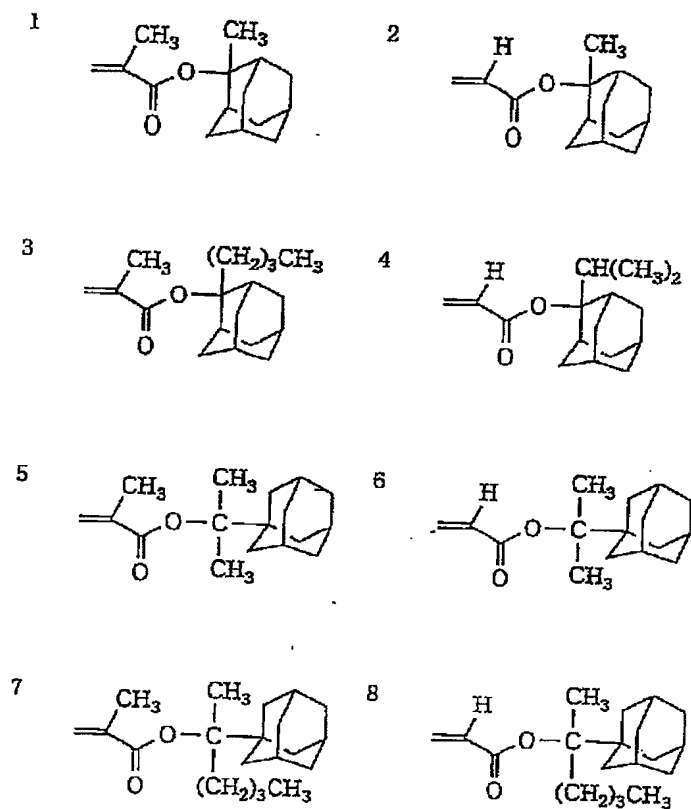


[0070] Inside of a general formula (pA); R expresses the permutation of a hydrogen atom, a halogen atom, or carbon numbers 1-4, an unsubstituted straight chain, or the alkyl group of branching. two or more R -- each -- even if the same, you may differ. The halogen atom of this R and an alkyl group can give the same example as R of the below-mentioned general formula (a). A' is synonymous with the above. R_a expresses

the radical of either above-mentioned formula (pI) – (pVI). The example of the monomer which is equivalent to the repeat unit shown by the general formula (pA) hereafter is shown.

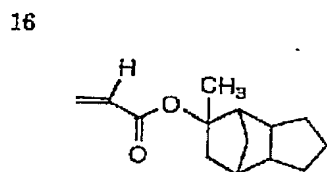
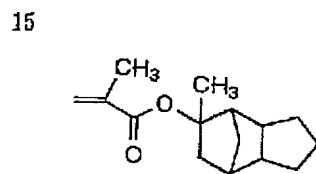
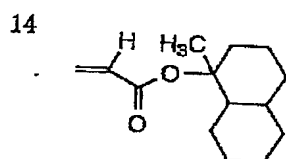
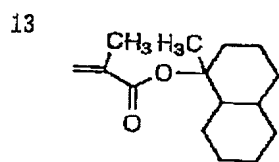
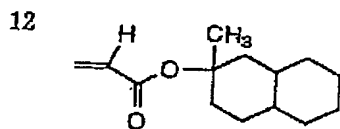
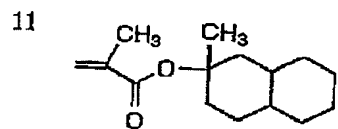
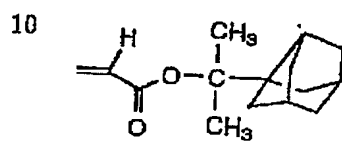
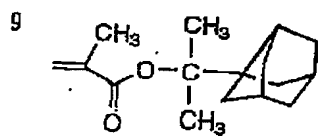
[0071]

[Formula 39]



[0072]

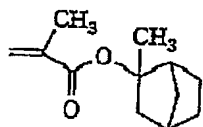
[Formula 40]



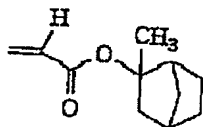
[0073]

[Formula 41]

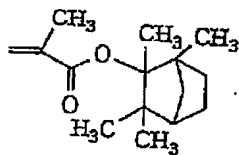
17



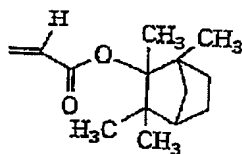
18



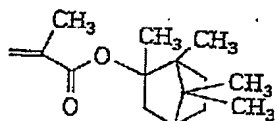
19



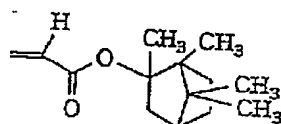
20



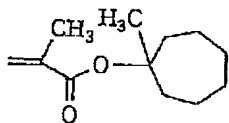
21



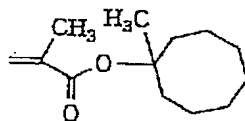
22



23



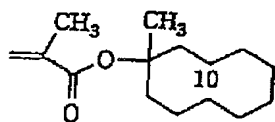
24



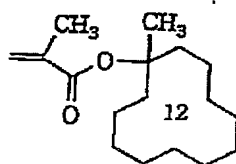
[0074]

[Formula 42]

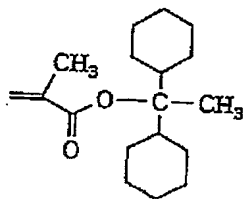
25



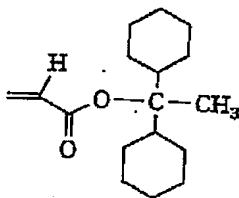
26



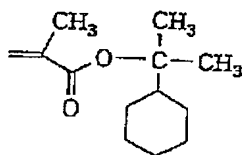
27



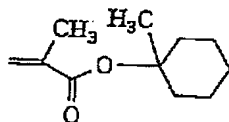
28



29

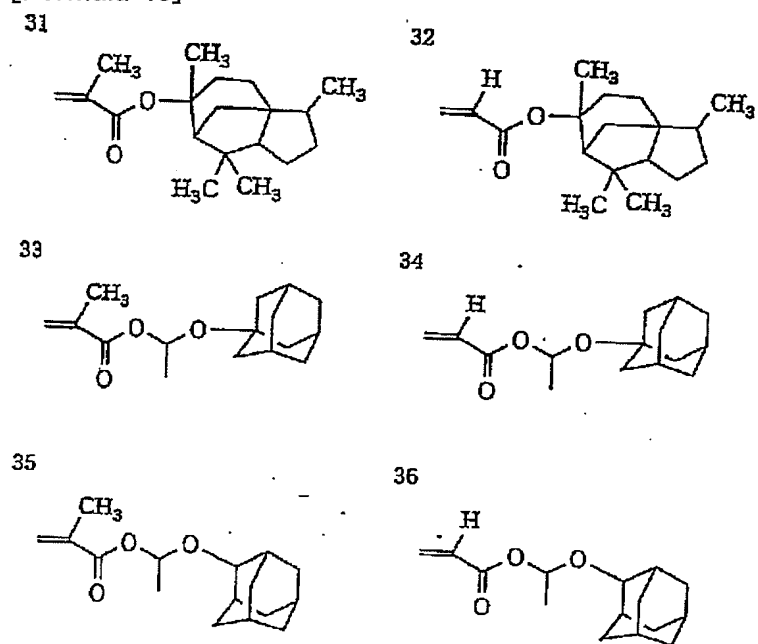


30



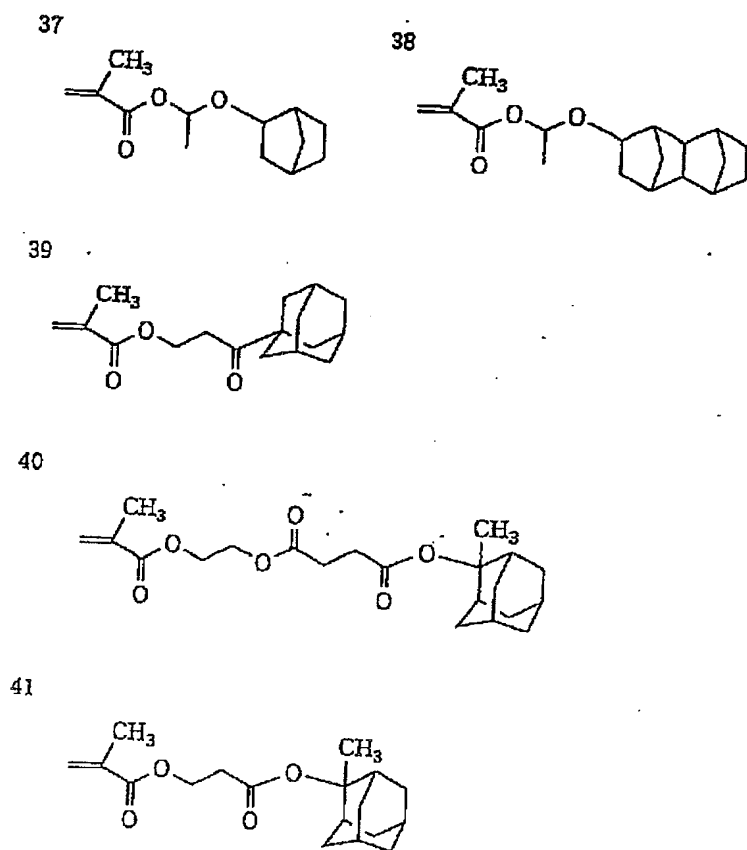
[0075]

[Formula 43]



[0076]

[Formula 44]



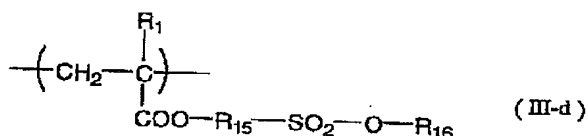
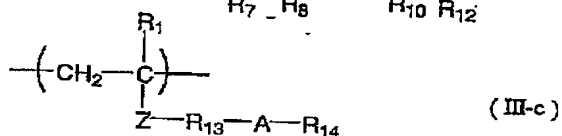
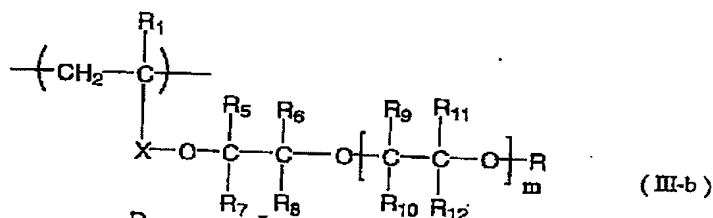
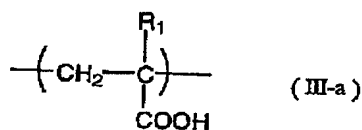
[0077] (B) Resin may also include the repeat unit of further others.

As for (B) resin in this invention, it is desirable to include the repeat unit shown by said general formula (a) as

other copolymerization components. Thereby, development nature and adhesion with a substrate improve. The example same as alkyl which may have the substituent of R in a general formula (a) as R1 in said general formula (I-1) – (I-4) can be given. As a halogen atom of R, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. At least one of R32–R34 of a general formula (a) is a hydroxyl group, it is a dihydroxy object and a mono-hydroxy object preferably, and is a mono-hydroxy object more preferably. Furthermore, as for (B) resin in this invention, it is desirable to include the repeat unit shown by following general formula (III-a) – (III-d) as other copolymerization components. Thereby, the resolution of a contact hole pattern improves.

[0078]

[Formula 45]

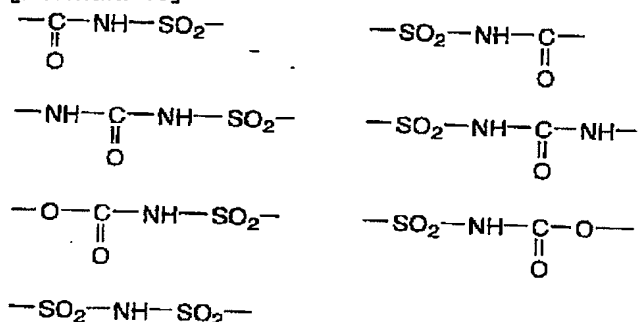


[0079] R1 is said R and homonymy among the above-mentioned formula. R5–R12 express the alkyl group which may have the hydrogen atom or the substituent independently respectively. R expresses the alkyl group and annular alkyl group which may have the hydrogen atom or the substituent, an aryl group, or an aralkyl radical. m expresses the integer of 1–10. At least two, the independence chosen from the group which consists of the alkylene group and annular alkylene group which may have single bond or a substituent, an arylene radical or a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, a urethane group, and an urea radical, or these radicals, or more are put together, and X expresses the divalent radical which is not decomposed according to an operation of an acid. Z expresses single bond, a ether group, an ester group, an amide group, an alkylene group, or the divalent radical that combined these. R13 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these. R15 expresses an alkylene group, an arylene radical, or the divalent radical that combined these. R14 expresses the alkyl group and annular alkyl group which may have the substituent, an aryl group, or an aralkyl radical. R16 expresses the alkyl group and annular alkyl group which may have the hydrogen atom or the substituent, an alkenyl radical, an aryl group, or an aralkyl radical. A expresses either of the

functional groups shown below.

[0080]

[Formula 46]



[0081] As an alkyl group of R5-R12, and R, R14 and R16, the alkyl group of the shape of a straight chain and the letter of branching is mentioned, and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the shape of a straight chain of 1-12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, a decyl group still more preferably As an annular alkyl group of R, R14, and R16, the thing of 3-30 carbon numbers is mentioned, and, specifically, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, etc. can be mentioned.

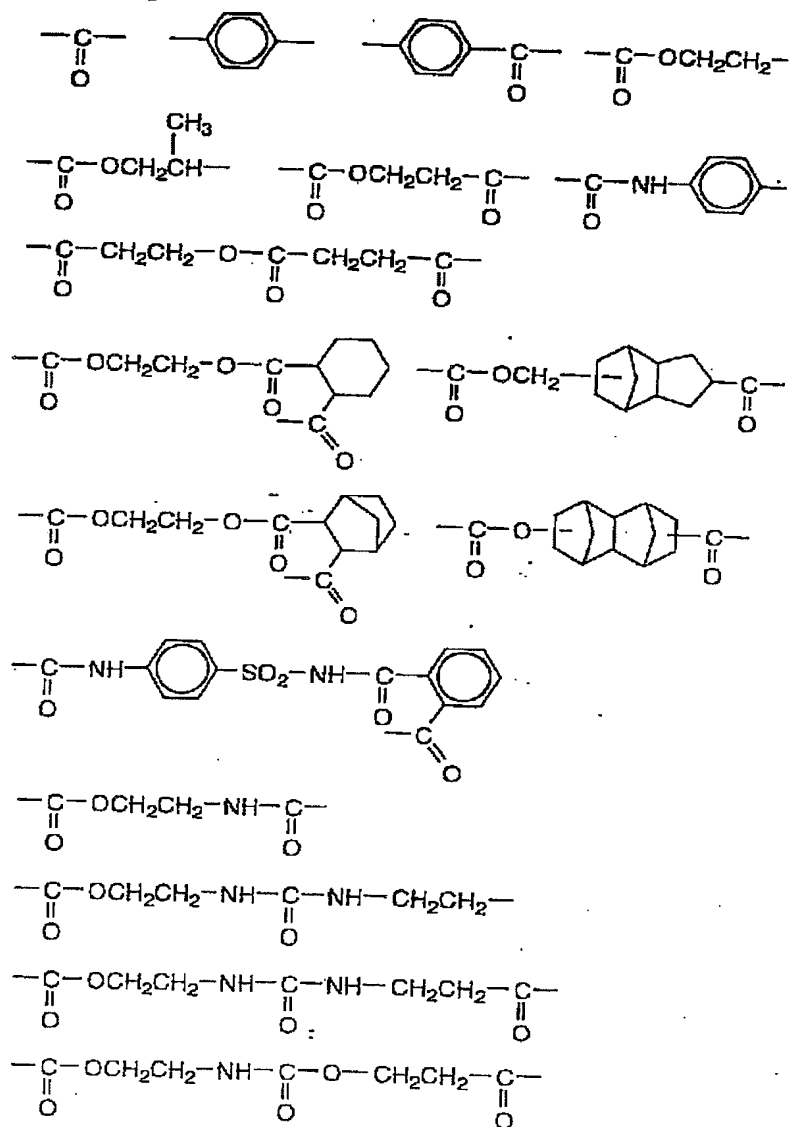
[0082] As an aryl group of R, R14, and R16, the thing of 6-20 carbon numbers is mentioned, and you may have the substituent. Specifically, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As an aralkyl radical of R, R14, and R16, the thing of 7-20 carbon numbers is mentioned, and the benzyl and the phenethyl radical which may have the substituent, a cumyl radical, etc. are mentioned. As an alkenyl radical of R16, the alkenyl radical of 2-6 carbon numbers is mentioned, and a vinyl group, a propenyl radical, an allyl group, a butenyl group, a pentenyl radical, a hexenyl radical, a cyclo pentenyl radical, a cyclohexenyl group, a 3-oxo-cyclohexenyl group, a 3-oxo-cyclo pentenyl radical, a 3-oxo-indenyl group, etc. are specifically mentioned. The annular alkenyl radical may contain the oxygen atom among these.

[0083] At least two, the independence chosen from the group which consists of the alkylene group and annular alkylene group which may have the substituent, an arylene radical or a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, a urethane group, and an urea radical as a connection radical X, or these radicals, or more are put together, and the divalent radical which is not decomposed according to an operation of an acid is mentioned. Z expresses single bond, a ether group, an ester group, an amide group, an alkylene group, or the divalent radical that combined these. R13 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these. R15 expresses an alkylene group, an arylene radical, or the divalent radical that combined these. In X, R13, and R15, the thing of 6-10 carbon numbers is mentioned as an arylene radical, and you may have the substituent.

Specifically, a phenylene group, a tolylene radical, a naphthylene radical, etc. are mentioned. As an annular alkylene group of X, that from which the above-mentioned annular alkyl group became divalent is mentioned. The radical expressed with the following type can be mentioned as an alkylene group in X, Z, R13, and R15. - Ra and Rb express a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group among a [C (Ra) and (Rb)] r1-type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r1 expresses the integer of 1-10. Although the example of the connection radical X is shown below, the contents of this invention are not limited to these.

[0084]

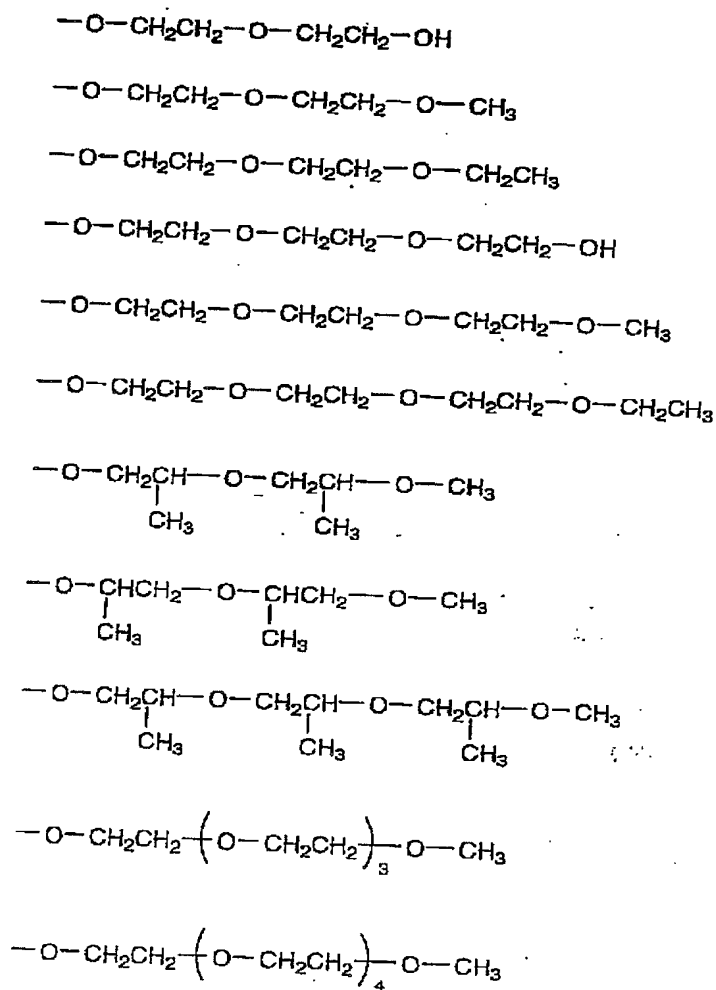
[Formula 47]



[0085] As further substituent in an above-mentioned alkyl group, annular alkyl group, and alkenyl radical, aryl group, aralkyl radical, alkylene group, annular alkylene group, and arylene radical, a carboxyl group, an acyloxy radical, a cyano group, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, an acetyl amide group, an alkoxy carbonyl group, and an acyl group are mentioned. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclo propyl group, cyclo butyl, and a cyclopentylic group, can be mentioned here. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. An acetoxyl radical etc. is mentioned as an acyloxy radical. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned.

[0086] Hereafter, although the example of the structure of the end except X is shown below as an example of the structure of the side chain in a general formula (III-b), the contents of this invention are not limited to these.

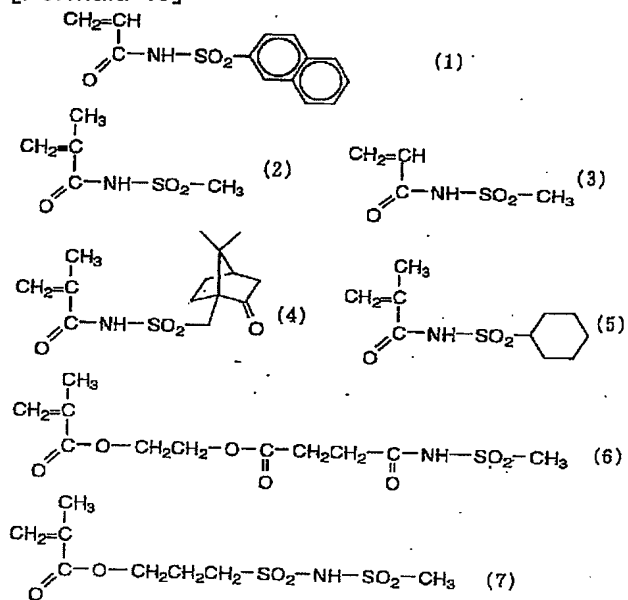
[Formula 48]



[0087] Although the example of the monomer which is equivalent to the repeat structural unit shown by the general formula (III-c) hereafter is shown, the contents of this invention are not limited to these.

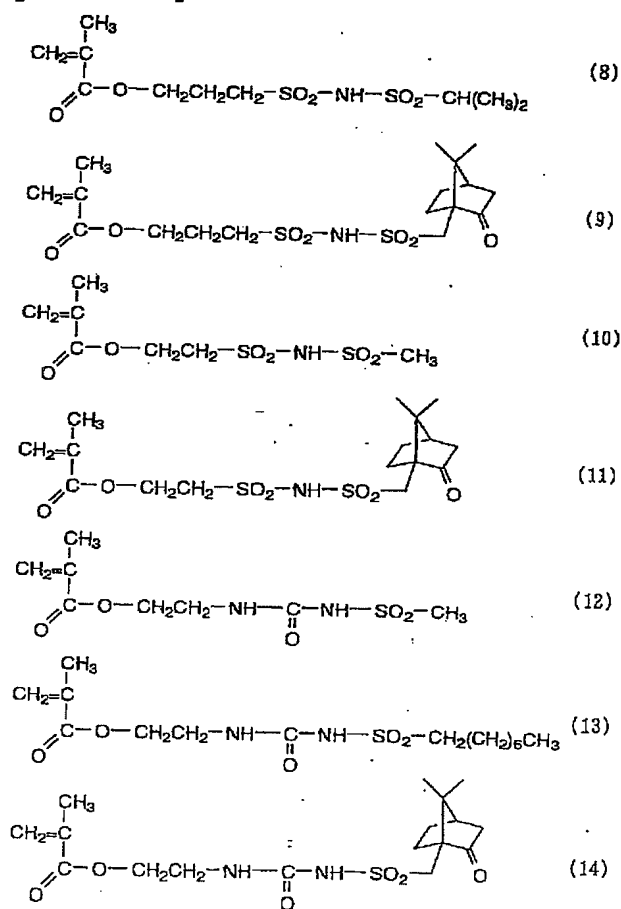
[0088]

[Formula 49]



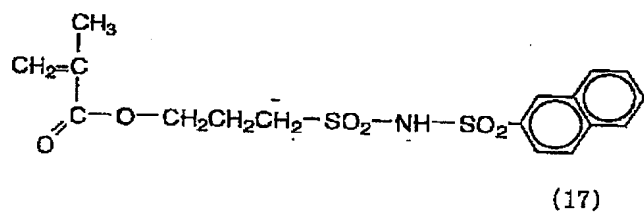
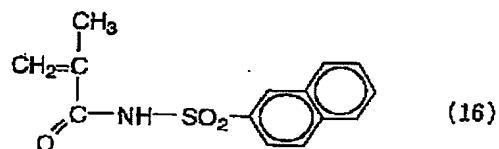
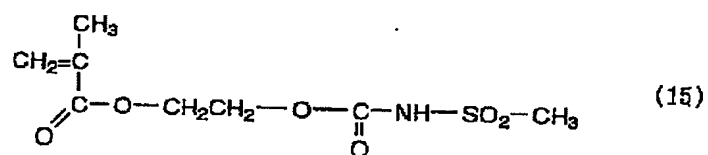
[0089]

[Formula 50]



[0090]

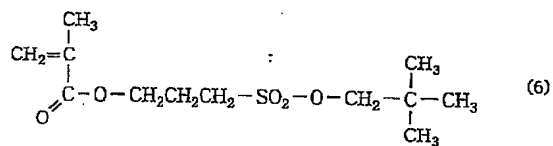
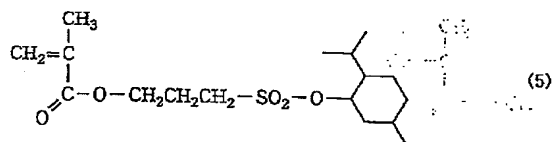
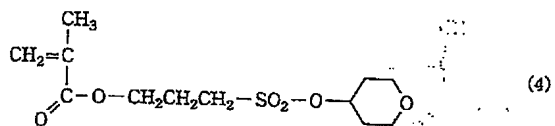
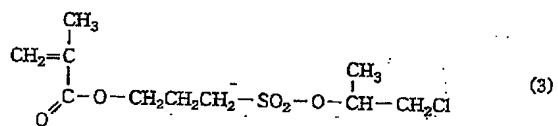
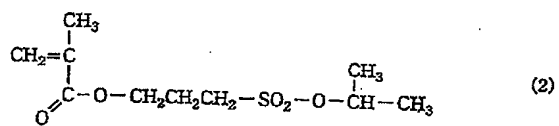
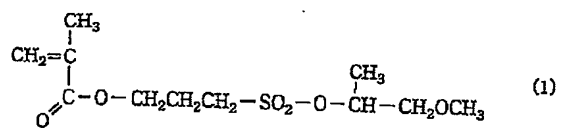
[Formula 51]



[0091] Although the example of the ** <TXF FR=0004 HE=005 WI=080 LX=1100 LY=2750> ***** structural unit shown by the general formula (III-d) is shown hereafter, the contents of this invention are not limited to these.

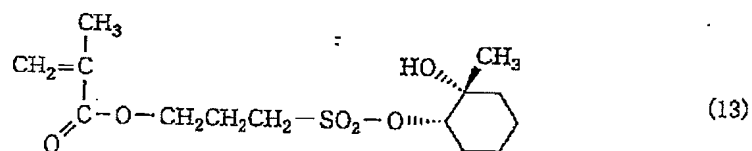
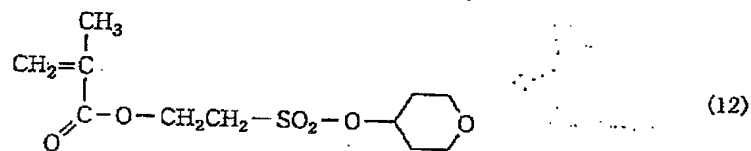
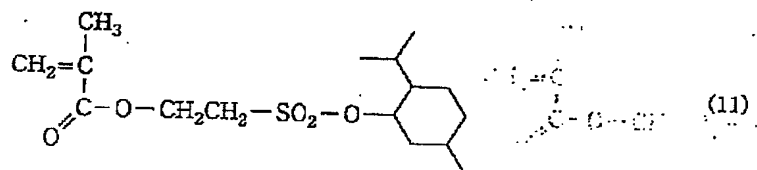
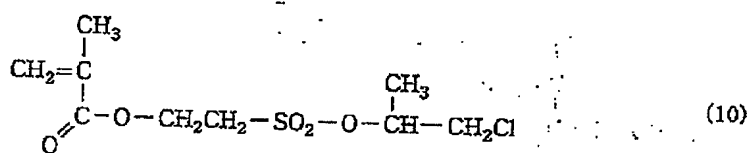
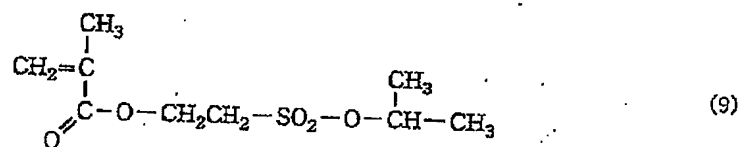
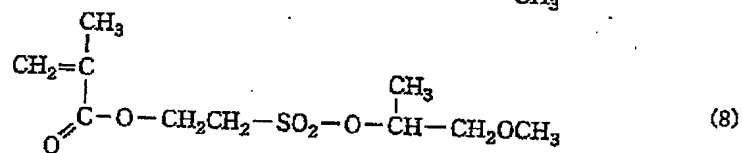
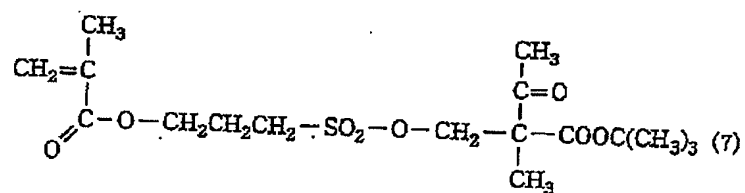
[0092]

[Formula 52]



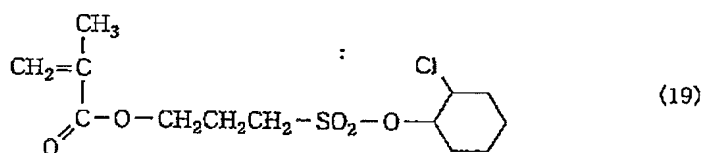
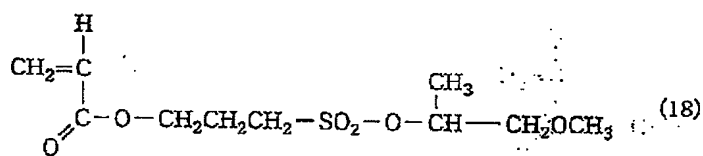
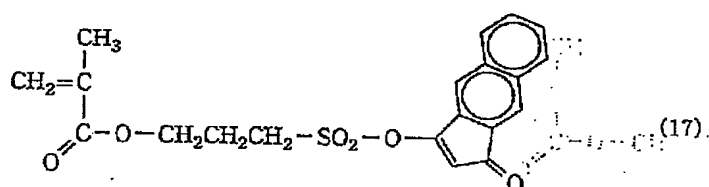
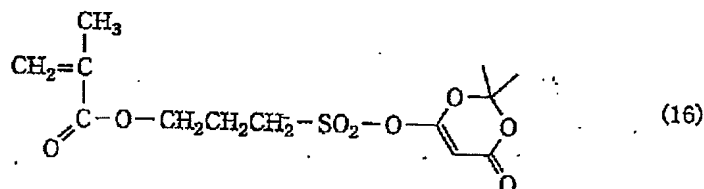
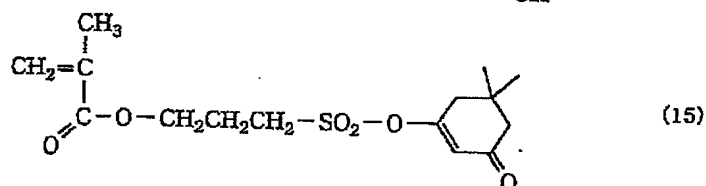
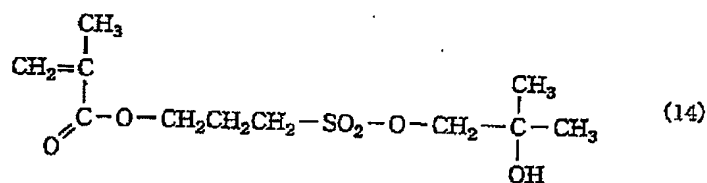
[0093]

[Formula 53]



[0094]

[Formula 54]



[0095] In a general formula (III-b), a hydrogen atom and a methyl group are desirable as R5-R12. As R, a hydrogen atom and the alkyl group of 1-4 carbon numbers are desirable. As for m, 1-6 are desirable. In a general formula (III-c), as R13, alkylene groups, such as single bond, a methylene group, ethylene, a propylene radical, and a butylene radical, are desirable, and annular alkyl groups, such as an alkyl group of 1-10 carbon numbers, such as a methyl group and an ethyl group, a cyclo propyl group, a cyclohexyl radical, and camphor residue, a naphthyl group, and a naphthyl methyl group are desirable as R14. Single bond, ether linkage, an ester bond, the alkylene groups of 1-6 carbon numbers, or those combination of Z are desirable, and it is single bond and an ester bond more preferably. In a general formula (III-d), the alkylene group of 1-4 carbon numbers is desirable as R15. As R16, the phenyl group and toluyl radical which may have the alkyl group of 1-8 carbon numbers, such as the methyl group and ethyl group which may have the substituent, a propyl group, an isopropyl group, butyl, a neopentyl radical, and an octyl radical, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, the menthyl radical, the morpholino radical, the 4-oxocyclohexyl radical, and the substituent, a mesityl radical a naphthyl group, and

camphor residue are desirable. As these further substituents, halogen atoms, such as a fluorine atom, the alkoxy group of 1-4 carbon numbers, etc. are desirable. The repeat unit shown by the general formula (III-b) and the general formula (III-d) also in a general formula (III-a) – a general formula (III-d) in this invention is desirable.

[0096] In addition to the above, further, the resin of (B) can be used as a copolymer with various monomer repeat units in order to adjust dry etching resistance, standard developer fitness and substrate adhesion, a resist profile, the resolution that is the general requisite of a resist, thermal resistance, sensibility, etc.

[0097] Although the repeat unit equivalent to the following monomers can be mentioned as such a repeat unit, it is not limited to these. Thereby, fine tuning of the adhesion to the substrate of the engine performance required of said resin, the solubility over (1) spreading solvent, (2) film-production nature (glass transition point), (3) alkali development property, (4) ***** (relative-degree-of-intimacy aquosity, alkali fusibility radical selection), and (5) unexposed parts and (6) dry-etching resistance ** is attained especially. The compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a copolymerization monomer, for example can be mentioned.

[0098] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic-acid propyl -- Acrylic-acid amyl, acrylic-acid cyclohexyl, acrylic-acid ethylhexyl, Acrylic-acid octyl, acrylic-acid-t-octyl, chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, etc.;

[0099] methacrylic ester (for example, methyl methacrylate --), for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10.) methacrylate Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl-3-hydroxypropyl methacrylate, Trimethylol propane mono-methacrylate, pentaerythritol mono-methacrylate, Furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.; Acrylamides For example, acrylamide, N-alkyl acrylamide (as an alkyl group, there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, a hydroxyethyl radical, etc.), N and N-dialkyl acrylamide (as an alkyl group, the carbon atomic numbers 1-10) for example, there are a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc.

N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0100] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as an alkyl group, the carbon atomic numbers 1-10) for example, there are a methyl group, an ethyl group, t-butyl, an ethylhexyl radical, a hydroxyethyl radical, a cyclohexyl radical, etc. N and N-dialkyl methacrylamide (as an alkyl group -- an ethyl group --) N-hydroxyethyl-N-methyl methacrylamide, such as a propyl group and butyl etc.; An allyl compound, for example, allyl ester (for example, an acetic-acid allyl compound, allyl caproate, and a caprylic-acid allyl compound --) A lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, Allyloxy ethanol, such as an acetoacetic-acid allyl compound and a

lactic-acid allyl compound etc.; Vinyl ether for example, alkyl vinyl ether (for example, hexyl vinyl ether and octyl vinyl ether --) DESHIRU vinyl ether, ethylhexyl vinyl ether, methoxy ethyl vinyl ether, Ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, the 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, hydroxyethyl vinyl ether, Diethylene-glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.;

[0101] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, Vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, Vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, Vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, ; itaconic-acids dialkyls (for example, dimethyl itaconate --), such as vinyl lactate, vinyl-beta-phenyl butyrate, and vinyl cyclohexyl carboxylate In addition to this, The dialkyl ester (for example, dibutylfumarate etc.) or monoalkyl ester of; boletic acid, such as itaconic-acid diethyl and dibutyl itaconate; An acrylic acid, A methacrylic acid, a crotonic acid, an itaconic acid, a maleic anhydride, maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc. can be mentioned. In addition, what is necessary is just the above-mentioned various repeat units and the unsaturated compound of copolymerizable addition polymerization nature. In the resin of (B), the content mole ratio of each repeat unit structure is suitably set up, in order to adjust the acid number, the dry etching resistance of a resist, standard developer fitness, substrate adhesion, the dependency of a resist profile of condensation and rarefaction, the resolution still more generally demanded to a resist, thermal resistance, sensibility, etc.

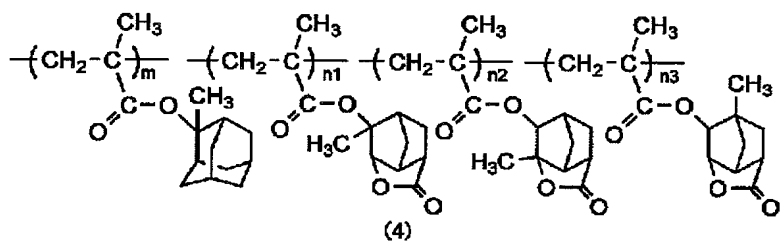
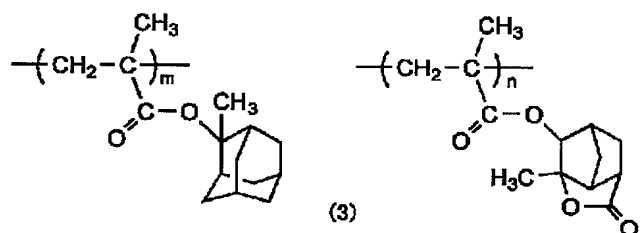
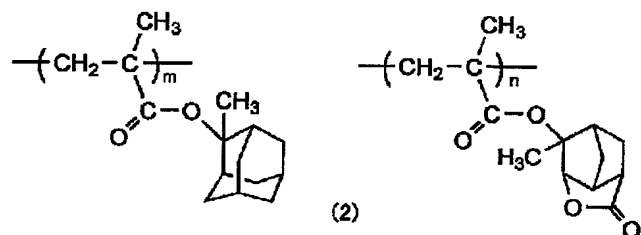
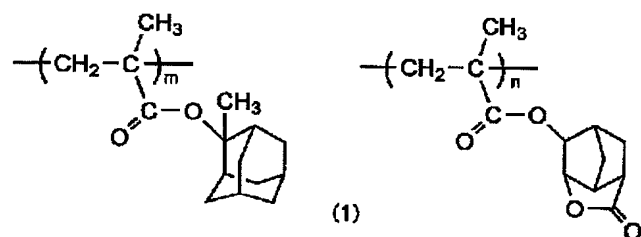
[0102] the content of the repeat unit which has the radical expressed with general formula (I-1) - (I-4) among the resin of (B) -- all 30 in repeat unit - 70-mol % -- it is -- desirable -- 35 - 65-mol % -- it is 40 - 60-mol % still more preferably. moreover, the content of the repeat unit which has the radical expressed with general formula (pI) - (pVI) -- all the inside of a repeat unit -- usually -- 20-75-mol % -- it is -- desirable -- 25-70-mol % -- it is 30-65-mol % still more preferably. (B) the content of the repeat unit expressed with a general formula (a) among resin -- usually -- all zero-mol % in monomer repeat unit - 70-mol % -- it is -- desirable -- 10 - 40-mol % -- it is 15 - 30-mol % still more preferably. moreover, the content of the repeat unit expressed with a general formula (III-a) - a general formula (III-d) among (B) resin -- usually -- all 0.1-mol % in monomer repeat unit - 30-mol % -- it is -- desirable -- 0.5 - 25-mol % -- it is 1 - 20-mol % still more preferably.

[0103] moreover, the account of a top, although the content in the resin of the repeat unit based on the monomer of the further copolymerization component can also be suitably set up according to the engine performance of a desired resist Less than [99 mol %] is desirable to the total number of mols which totaled the repeat unit which has the radical expressed with the repeat unit which generally contains the radical expressed with a general formula (I-1) - (I-4) either and general formula (pI) - (pVI). It is less than [80 mol %] preferably [it is more desirable and] to a 90 mol % less or equal and a pan. the weight average molecular weight Mw of the resin of (B) -- the gel-permeation-chromatography method -- a polystyrene criterion -- it is -- desirable -- 1,000-1,000,000 -- more -- desirable -- 1,500-500,000 -- further -- desirable -- 2,000-200,000 -- especially, it is the range of 2,500-100,000 preferably, and while its thermal resistance etc. improves so that weight average molecular weight is large, development nature etc. falls and it is adjusted to the desirable range by these balance. The resin of (B) used for this invention is compoundable by the radical polymerization method according to a conventional method. Hereafter, although the example of the resin of (B) of this invention is given, the contents of this invention are not limited to

these.

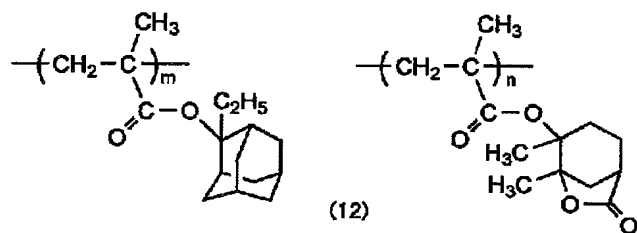
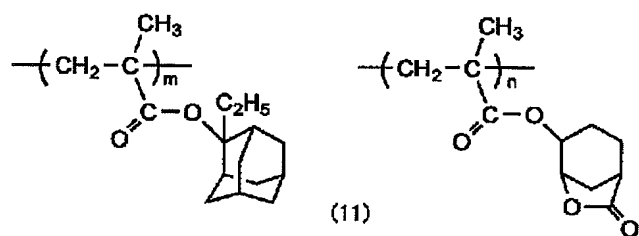
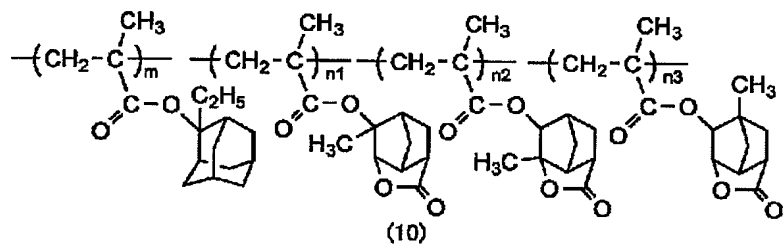
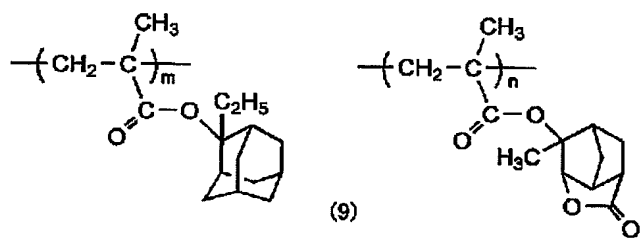
[0104]

[Formula 55]



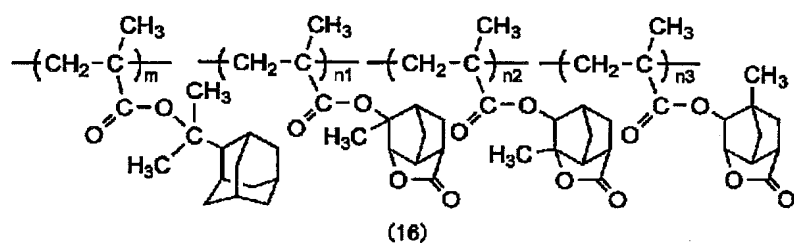
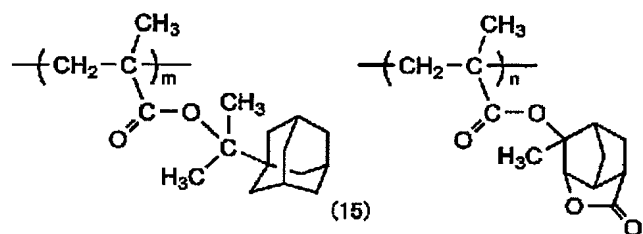
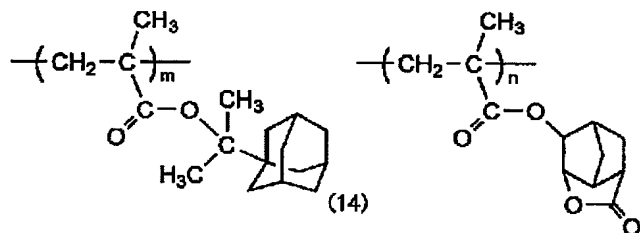
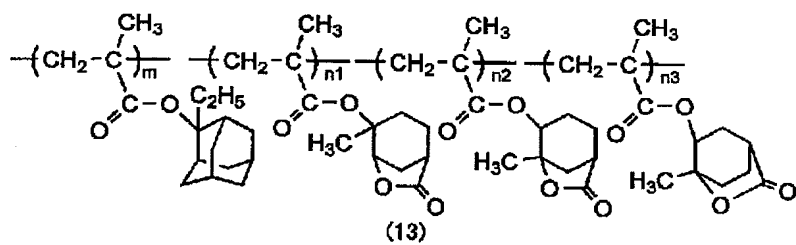
[0105]

[Formula 56]



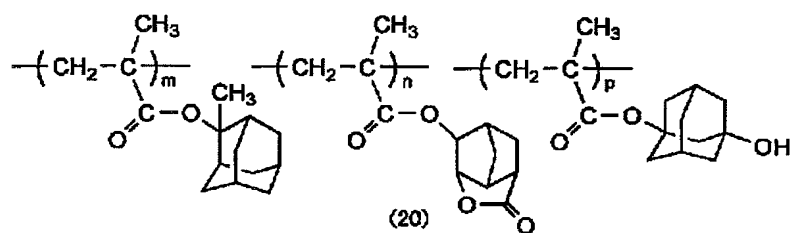
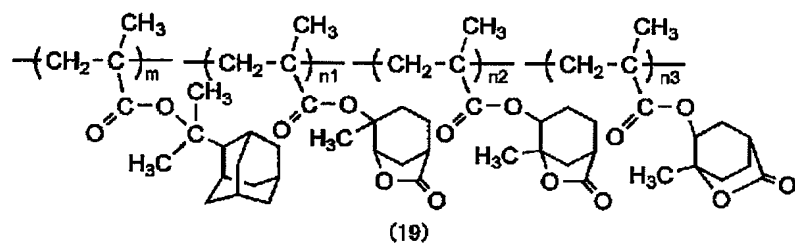
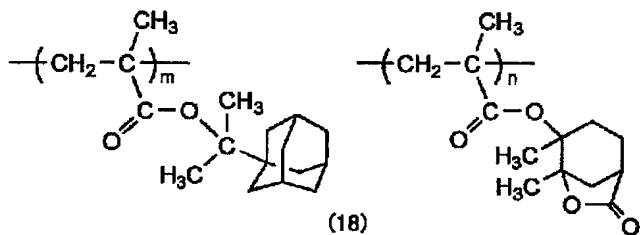
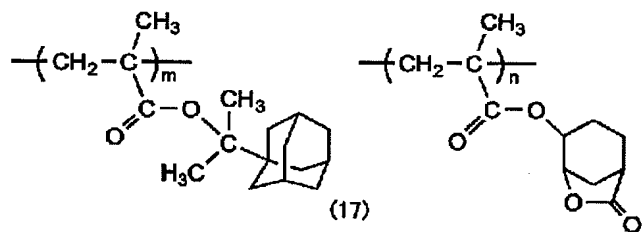
[0107]

[Formula 58]



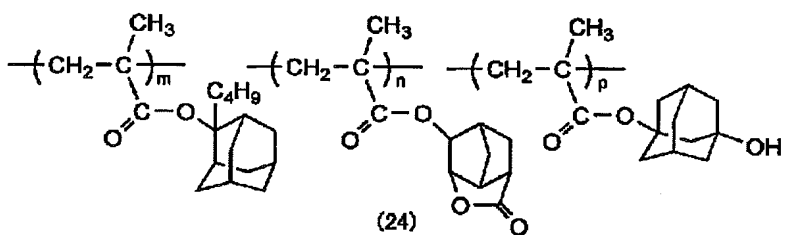
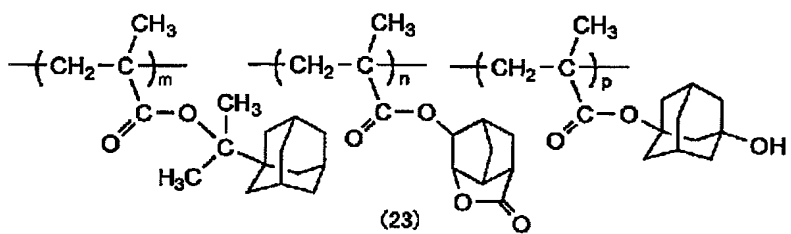
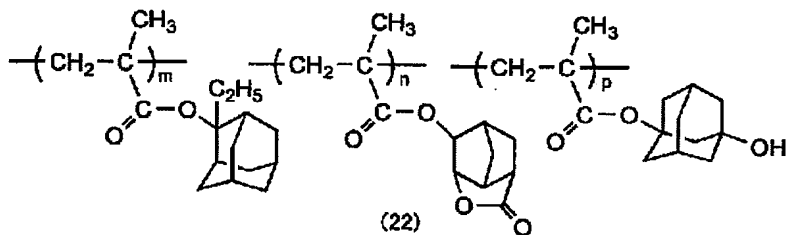
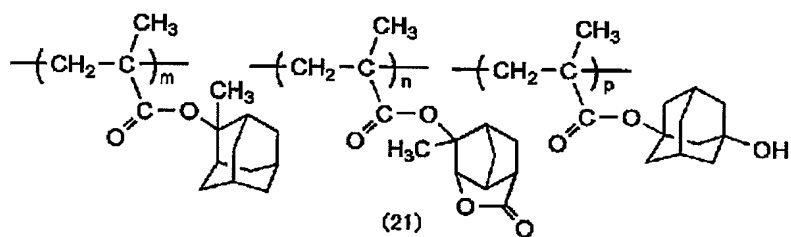
[0108]

[Formula 59]



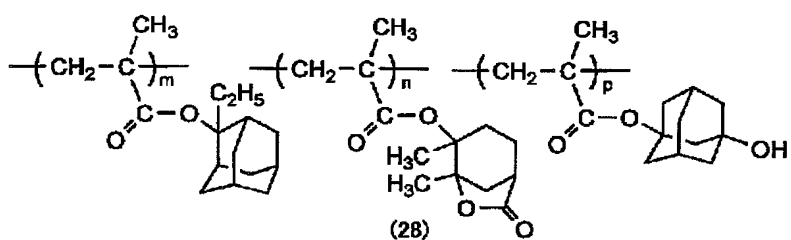
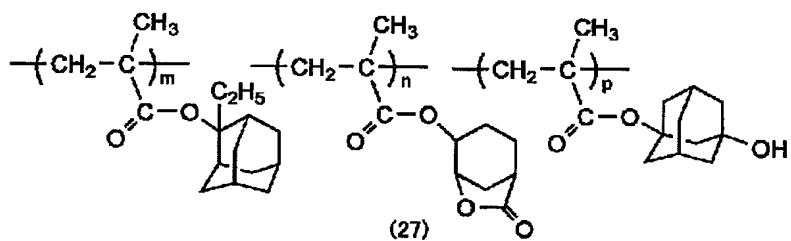
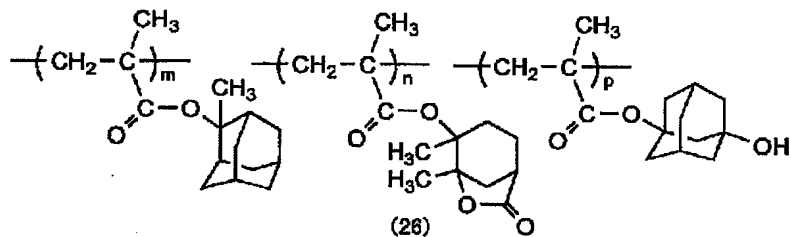
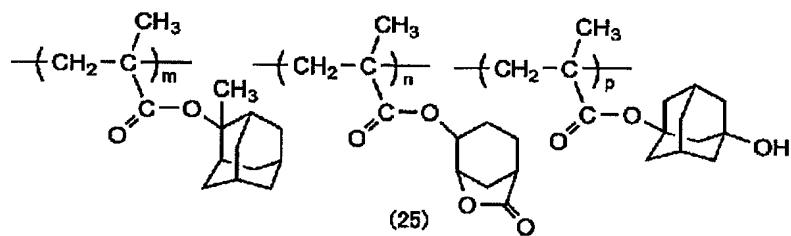
[0109]

[Formula 60]



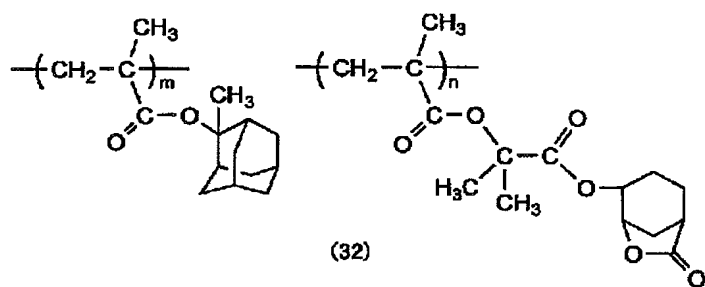
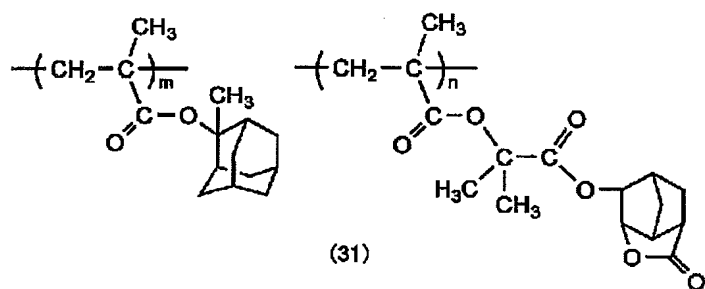
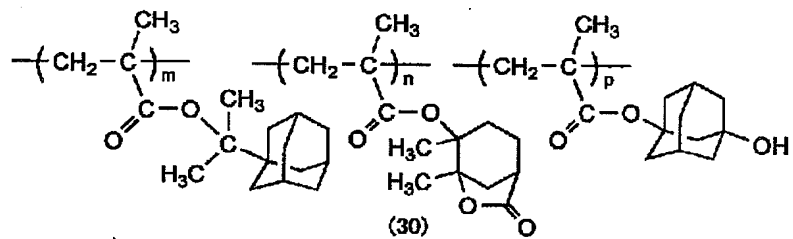
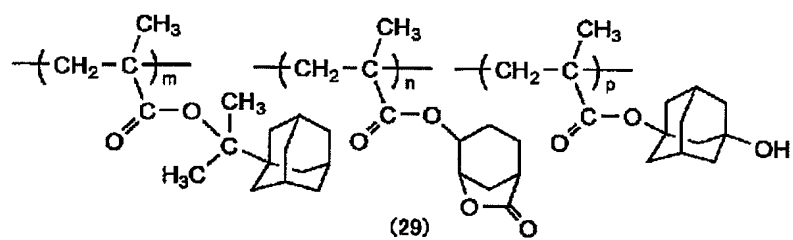
[0110]

[Formula 61]



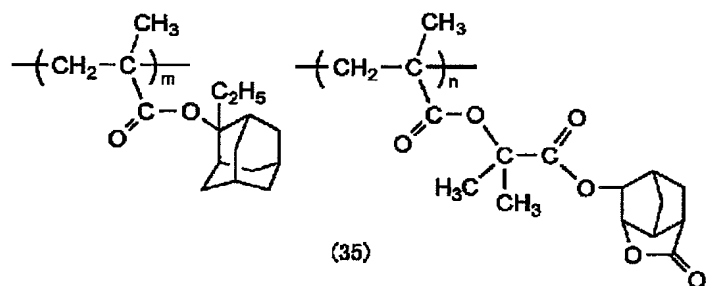
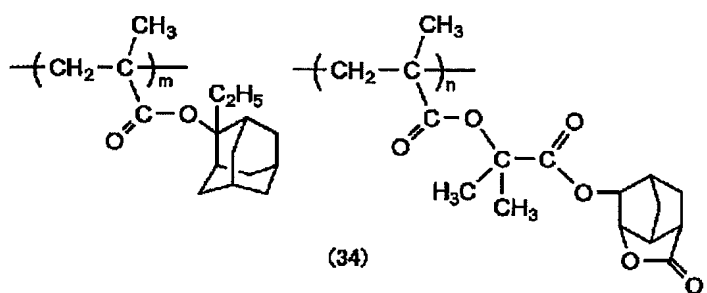
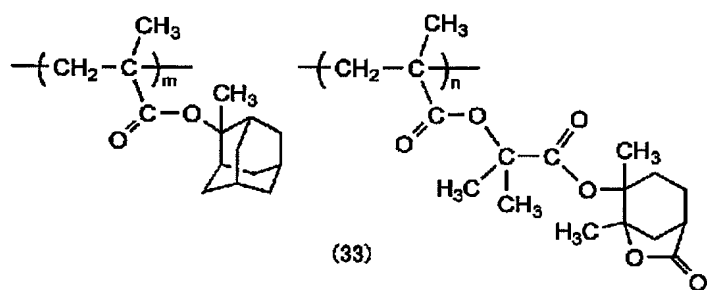
[0111]

[Formula 62]



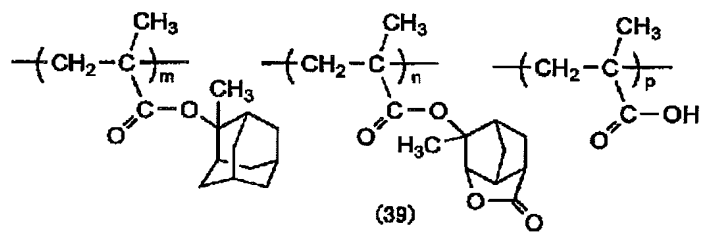
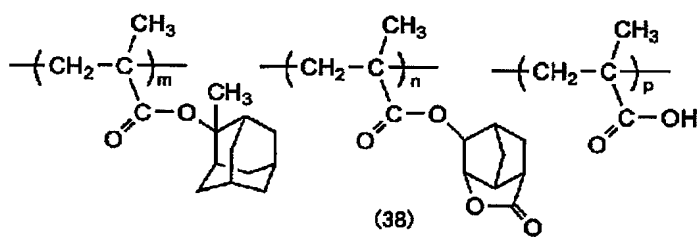
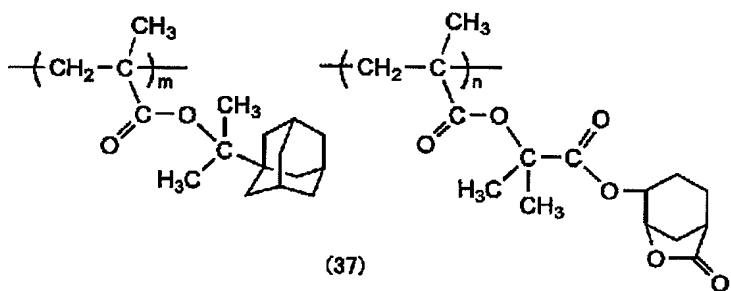
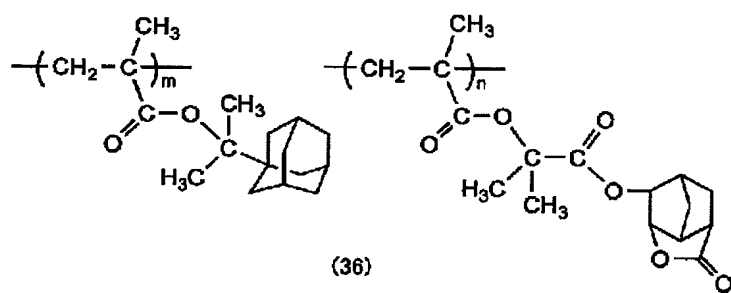
[0112]

[Formula 63]



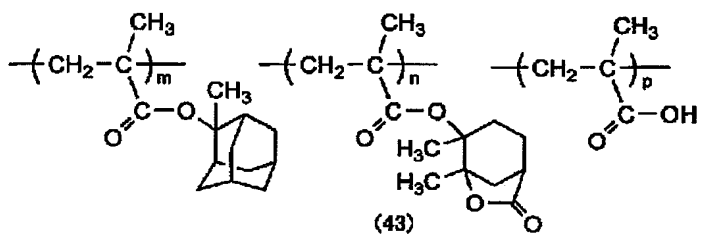
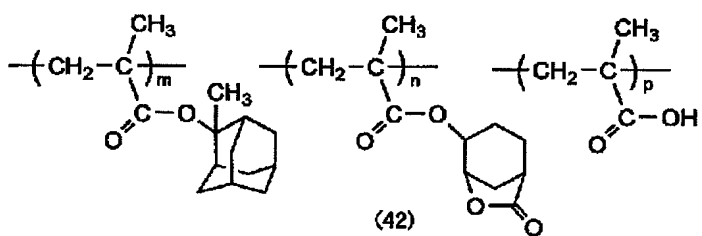
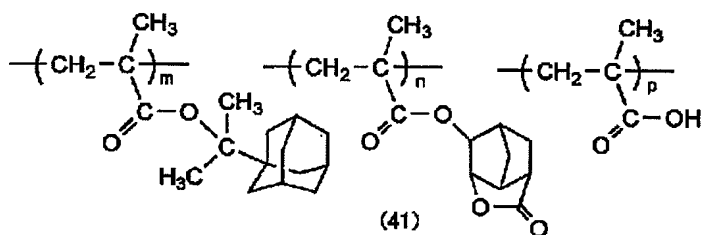
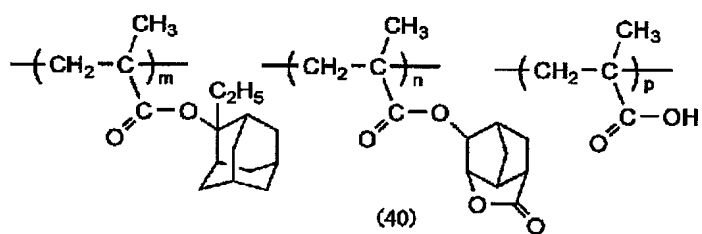
[0113]

[Formula 64]



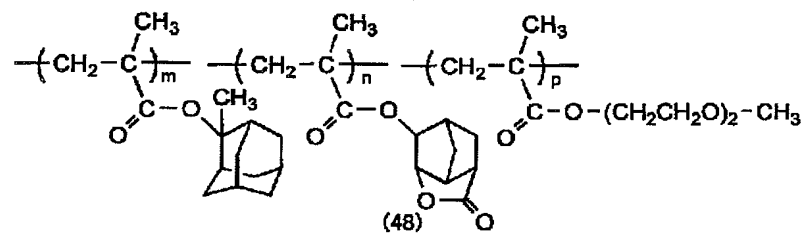
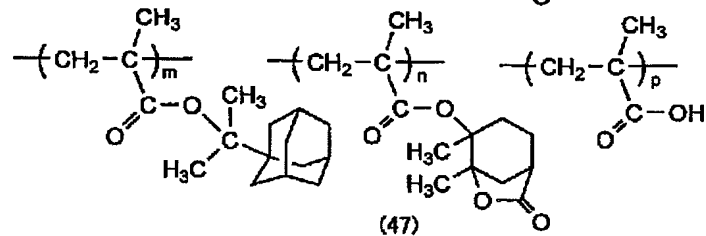
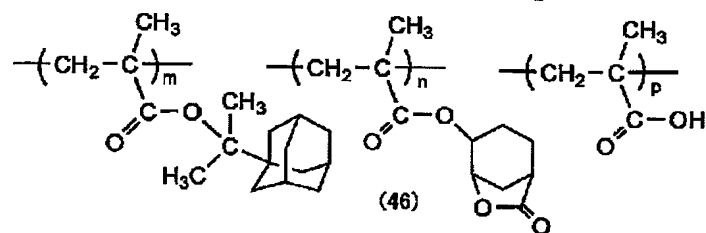
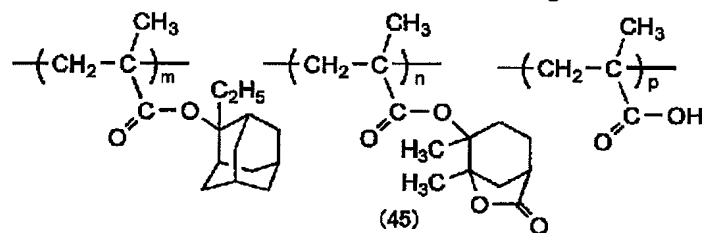
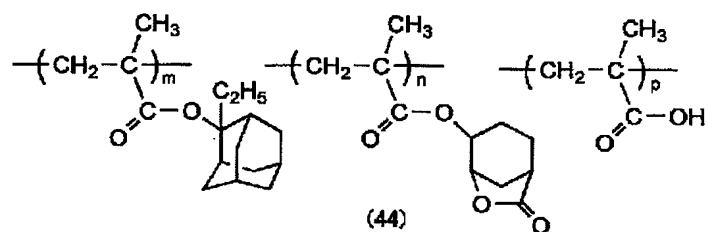
[0114]

[Formula 65]



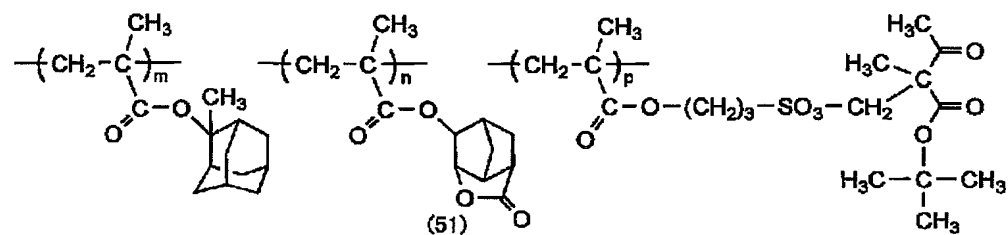
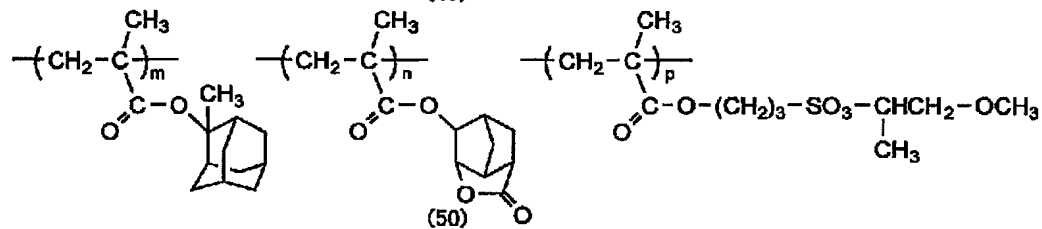
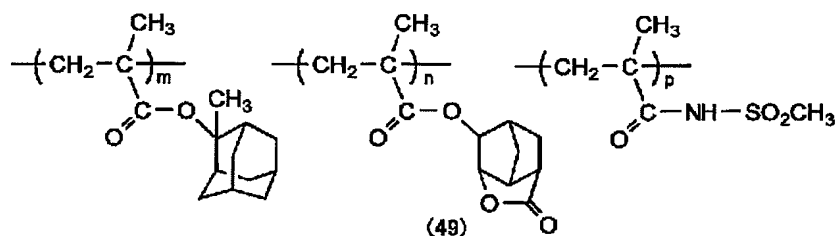
[0115]

[Formula 66]



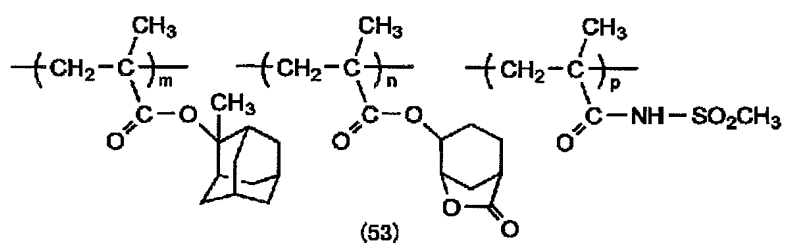
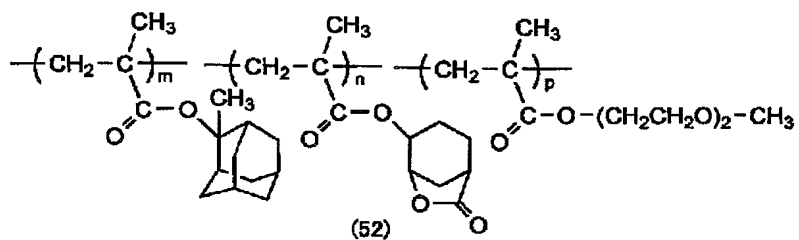
[0116]

[Formula 67]



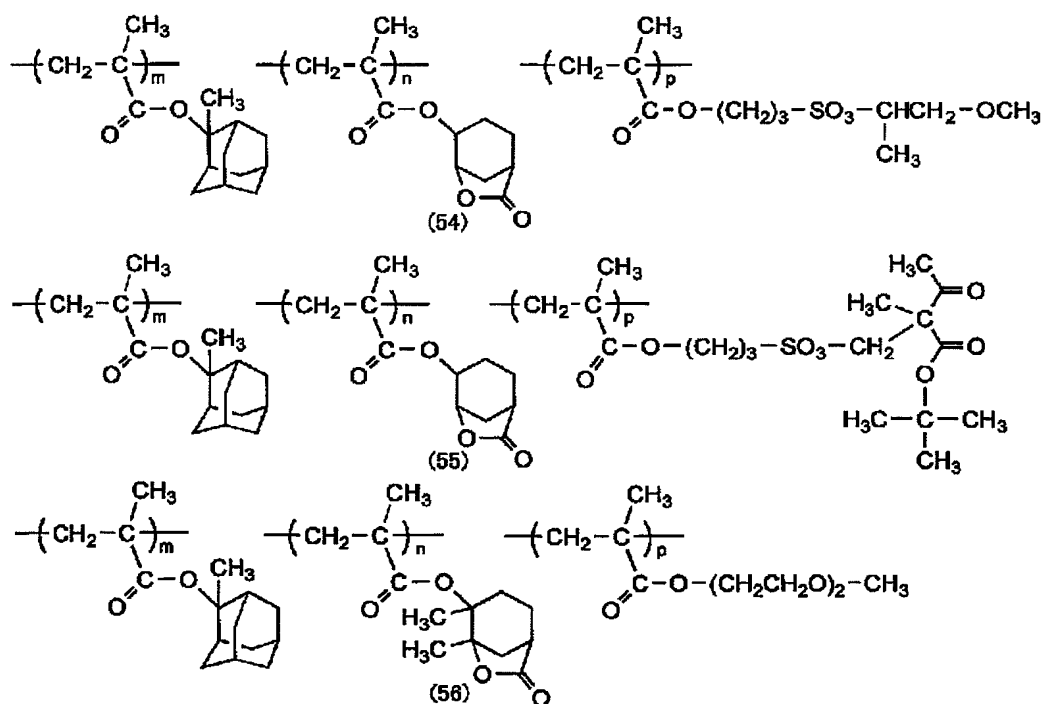
[0117]

[Formula 68]



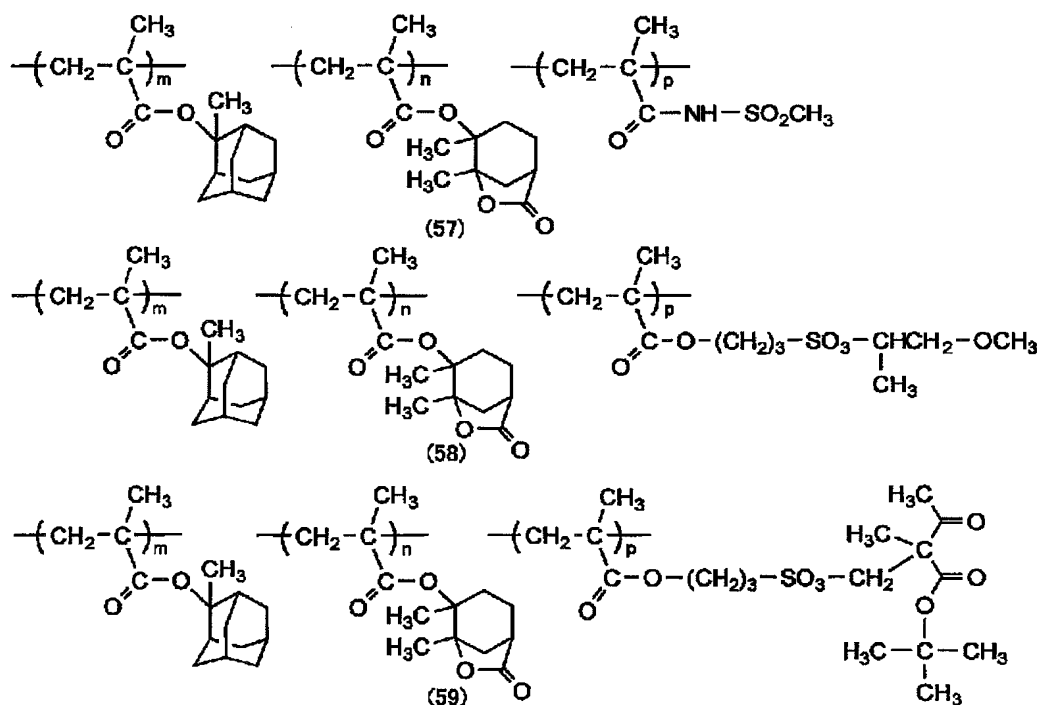
[0118]

[Formula 69]



[0119]

[Formula 70]



[0120] m, n, p, and n₁, n₂ and n₃ show the mole ratio of a number [each] among the above-mentioned formula. (I-1) n showed the repeat unit which has the radical expressed with either of (I-4), and the case where two or more sorts were combined was distinguished by n₁, n₂, etc. m showed the repeat unit which has a radical including the alicyclic hydrocarbon structure expressed with (pI) - (pVI). p showed the repeat

unit shown by general formula (III-a) – (III-d). When it includes the repeat unit shown by general formula (III-a) – (III-d), m/n/p is (25–70)/(25–65)/(3–40). When it does not include the repeat unit shown by general formula (III-a) – (III-d), m/n is (30–70)/(70–30). A block copolymer or a random copolymer is sufficient. A regular polymer is sufficient and an irregular polymer is sufficient. In the positive type photoresist constituent for far-ultraviolet-rays exposure of this invention, among [all] resist solid content, the addition in the whole constituent of the resin of (B) has 40 – 99.99 desirable % of the weight, and is 50 – 99.97 % of the weight more preferably.

[0121] The positive-resist constituent of this invention can be made to contain further an acidolysis nature lysis inhibition compound, a color, a plasticizer, a surfactant, a photosensitizer, an organic base nature compound, the compound that promotes the solubility over a developer if needed. In the positive type photoresist constituent of this invention, a fluorine system and/or a silicon system surfactant may be contained. In the positive type photoresist constituent of this invention, either of the surfactants containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom or two sorts or more can be contained. As these surfactants, a surfactant JP,62–36663,A, JP,61–226746,A, JP,61–226745,A, JP,62–170950,A, JP,63–34540,A, JP,7–230165,A, JP,8–62834,A, JP,9–54432,A, and given in JP,9–5988,A can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, a fluorochemical surfactant or silicon system surfactants, such as EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), Sir chlorofluocarbon S–382, and SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), can be mentioned. Moreover, polysiloxane polymer KP–341 (Shin–Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0122] The loadings of a surfactant are usually 0.01 % of the weight – 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. You may add independently and these surfactants can also be added in some combination. As a surfactant which can be used above etc. Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate, etc. can be mentioned. The loadings of other surfactants of these are usually below 1 weight section preferably below 2 weight sections per solid content 100 weight section in the constituent of this invention.

[0123] As for (D) acid diffusion inhibitor which can be used by this invention, it is desirable to add at the point which controls fluctuation of exposure afterbaking and the sensibility in the passage of time to a development, and resolution, and it is an organic base nature compound preferably. The nitrogen-containing basicity compound with which an organic base nature compound has the following structures is mentioned.

[0124]

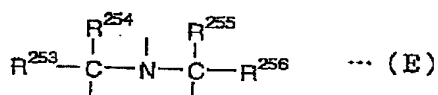
[Formula 71]



[0125] It is the permutation or the unsubstituted aryl group of that R250, R251, and R252 are the same, or a difference, a hydrogen atom, the alkyl group of carbon numbers 1-6, the amino alkyl group of carbon numbers 1-6, the hydroxyalkyl radical of carbon numbers 1-6 or carbon numbers 6-20, and it may join together mutually and R251 and R252 may form a ring here.

[0126]

[Formula 72]



[0127] (R253, R254, R255, and R256 show the alkyl group of the same, or a difference and carbon numbers 1-6 among a formula)

Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [a permutation or] preferably. As a desirable example, the aminopyridine which is not permuted [the guanidine which is not permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [in DAZORU which is not permuted / a permutation or /, a permutation or], The pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group. As a desirable concrete compound, guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino

pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, 1, a 5-diazabicyclo [4, 3, 0] nona-5-en, 1, a 8-diazabicyclo [5, 4, 0] undeca-7-en, 2, 4, 5-triphenyl imidazole, N-methyl morpholine, N-ethyl morpholine, The 3rd class morpholine derivatives, such as N-hydroxyethyl morpholine, N-benzyl morpholine, and cyclohexyl morpholino ethyl thiourea (CHMETU), Although the hindered amine (for example, thing given in this official report [0005]) of a publication is mentioned to JP,11-52575,A, it is not limited to this. Especially a desirable example 1, 5-diazabicyclo [4.3.0]-5-nonene, 1, 8-diazabicyclo [5.4.0]-7-undecene, 1, 4-diazabicyclo [2.2.2] octane, 4-dimethylaminopyridine, hexamethylenetetramine, 4, and 4-dimethyl imidazoline, Hindered amine, such as the 3rd class morpholines, such as pyrroles, pyrazoles, imidazole derivatives, pyridazines, pyrimidines, and CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO, can be mentioned. Especially, 1, 5-diazabicyclo [4, 3, 0] nona-5-en, 1, 8-diazabicyclo [5, 4, 0] undeca-7-en, 1, and 4-diazabicyclo [2, 2, 2] octane, 4-dimethylaminopyridine, a hexamethylenetetramine, CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO are desirable.

[0128] These nitrogen-containing basicity compounds are independent, or are combined two or more sorts and used. (D) The amount of the acid diffusion control agent (for example, nitrogen-containing basicity compound) used is usually 0.01 - 5 % of the weight preferably 0.001 to 10% of the weight to the solid content of all the constituents of a photopolymer constituent. At less than 0.001 % of the weight, the effectiveness of addition of the above-mentioned nitrogen-containing basicity compound is not acquired. On the other hand, when it exceeds 10 % of the weight, there is an inclination for the development nature of the fall of sensibility or a non-exposed area to get worse.

[0129] The positive-resist constituent of <(C) Solvent> this invention is melted to the solvent which dissolves each above-mentioned component, and is applied on a base material. In this invention, the solvent shown in the 1st solvent of (C) below is mixed, and it is used as all solvents. As a solvent to mix, ethylene dichloride, a cyclohexanone, Cyclopentanone, gamma-butyrolactone, a methyl ethyl ketone, methyl amyl ketone, Methyl isobutyl ketone, octanone 3, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, Ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, Toluene, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, Isobutyl acetate, methyl lactate, ethyl lactate, lactic-acid propyl, butyl lactate, Methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, N and N, N', N'-tetramethyl urea, It is desirable, and these solvents are added to (C), and N-methyl pyrrolidone, a tetrahydrofuran, ethylene carbonate, propylene carbonate, beta-methoxy isobutyric-acid methyl, ethyl butylate, butanoic acid propyl, at least one sort of diacetone alcohol, etc. are mixed, and use them.

[0130] Also in the above, gamma-butyrolactone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, the

propylene glycol monoethyl ether, methyl lactate, ethyl lactate, N-methyl pyrrolidone, methyl amyl ketone, octanone 3, butyl acetate, isobutyl acetate, methyl pyruvate, pyruvic-acid ethyl, and a tetrahydrofuran can be mentioned as a desirable solvent mixed to the 1st solvent of (C). The amount of the 1st solvent used of (C) is 70 – 85 % of the weight still more preferably 65 to 85% of the weight preferably 60 to 90% of the weight to all solvents. Such a positive-resist constituent of this invention is applied on a substrate, and forms a thin film. The thickness of this paint film has desirable 0.2–1.2 micrometers. In this invention, inorganic [commercial] or an organic antireflection film can be used as occasion demands. As antireflection film, inorganic membrane types, such as titanium, a titanium dioxide, titanium nitride, chromic oxide, carbon, and alpha-silicon, and the organic membrane type which consists of an extinction agent and a polymer ingredient can use. The former needs a facility of a vacuum evaporation system, a CVD system, a sputtering system, etc. for film formation. As organic antireflection film, for example The condensation product of a diphenylamine derivative given in JP,7-69611,B, and formaldehyde denaturation melamine resin, The thing, the maleic-anhydride copolymer given in U.S. Pat. No. 5294680, and the reactant of a diamine mold extinction agent which consist of alkali fusibility resin and an extinction agent, The thing containing a resin binder given in JP,6-118631,A, and a methylol melamine system heat cross linking agent, The acrylic resin mold antireflection film which has a carboxylic-acid radical, an epoxy group, and an extinction radical given in JP,6-118656,A in the same intramolecular, What consists of a methylol melamine given in JP,8-87115,A and a benzophenone system extinction agent, the thing which added the low-molecular extinction agent to polyvinyl alcohol resin given in JP,8-179509,A are mentioned. Moreover, DUV30 series by BURYUWA Saiensu-Sha, AC-2 of DUV-40 series and the product made from SHIPURE, AC-3, etc. can also be used as organic antireflection film.

[0131] On a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device, the above-mentioned resist liquid can be exposed through a predetermined mask after spreading by the suitable methods of application, such as a spinner and a coating machine, (on the substrate which was able to prepare the above-mentioned antireflection film as occasion demands), and a good resist pattern can be obtained by developing negatives by performing BEKU. As an exposure light, it is light with a wavelength of 150nm – 250nm preferably here. Specifically, a KrF excimer laser (248nm), an ArF excimer laser (193nm), F2 excimer laser (157nm), an X-ray, an electron beam, etc. are mentioned. As a developer, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline water solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, a pyrrole, and PIHERIJIN, can be used. Furthermore, alcohols and a surfactant can also be used for the alkaline above-mentioned water solution, carrying out suitable amount addition.

[0132]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples.

Synthetic example 1. The synthetic 2-methyl-2-adamanthyl methacrylate of the example of resin of this

invention (1) and the 5-exo-methacrylate of 6-endo-hydroxy bicyclo [2.2.1]

heptane-2-endo-carboxylic-acid-gamma-lactone were taught at a rate of mole ratios 50/50, it dissolved in N,N-dimethylacetamide / tetrahydrofuran =5/5, and 100ml of solutions of 20% of solid content concentration was adjusted. The 5-exo-methacrylate of 6-endo-hydroxy bicyclo [2.2.1]

heptane-2-endo-carboxylic-acid-gamma-lactone is acetoxo about a 6-endo-hydroxy bicyclo [2.2.1]

heptane-2-endo-carboxylic acid. - After lactonizing, alkali hydrolysis of the acetoxo radical was carried out at the hydroxy group, and what was compounded by esterifying by methacrylic-acid chloride further was used. J. It was based on the approach of Chem.Soc., 227 (1959), Tetrahedron, 21, and 1501 (1965)

publications. this solution -- the product V-65 made from the Wako Pure Chem industry -- three-mol% -- in addition, this was dropped at 10ml of N,N-dimethylacetamide heated at 60 degrees C over 3 hours under nitrogen-gas-atmosphere mind. after dropping termination and reaction mixture -- 3-hour heating -- again, 1mo1% addition was carried out and V-65 was agitated for 3 hours. Reaction mixture was cooled to the room temperature after reaction termination, and crystallization and the white fine particles which deposited were collected to distilled water 3L. The polymer presentation searched for from C13NMR was 51/49. Moreover, the weight average molecular weight of the standard polystyrene conversion for which it asked by GPC measurement was 7,200.

[0133] The resin 2-10 of the presentation ratio and molecular weight which are shown in Table 1 was ****(ed) like the synthetic examples 2-10 and the example 1 of synthetic composition of the resin of this invention.

[0134]

[Table 1]

合成例	本発明の樹脂 (樹脂例No)	組成比 (モル比) m/n 又は m/n/p	分子量
2	(5)	52/48	8,400
3	(6)	50/50	10,200
4	(8)	52/48	8,500
5	(17)	49/51	7,600
6	(20)	49/31/20	12,500
7	(28)	51/28/21	9,700
8	(38)	47/45/8	8,900
9	(45)	46/44/10	9,300
10	(54)	50/43/7	7,100

[0135] According to the synthesis method of a page [8th] publication of synthetic JP,10-274852,A of the example of a comparison (resin A4), as A4, it is the following, and the compound of a publication was made and compounded in this official report. Methacrylic-acid 2-methyl-2-adamantyl and alpha-meta-KURIRO yloxy-gamma-butyrolactone were taught by the mole ratio (40.0g : 29.0g) of 50:50, twice [2 weight] as many methyl isobutyl ketone as all monomers was added, and it considered as the solution. there -- as an initiator -- azobisisobutyronitril -- the total amount of monomers -- receiving -- two-mol % -- it added and heated

at 80 degrees C for about 8 hours. Then, actuation of having filled a lot of heptanes with reaction mixture, and settling it was performed twice, and was refined. Consequently, the copolymer shown by the degree type was obtained. The presentation mole ratio of each unit was 50:50, and weight average molecular weight was about 8,000.

[0136] [An example 1 – 10 and the example of a comparison]

0.03g [of photo-oxide generating agents] (PAG 4-36) and 4-dimethylaminopyridine 1.5mg and megger fuck F-176 (Dainippon Ink make) 0.05g are blended with 1.4g of resin compounded in adjustment of a photosensitive constituent and the example of the [evaluation] above-mentioned composition, and it is solid content 14w. After dissolving in the solvent indicated to Table 2 at t% of a rate, it filtered by the 0.1-micrometer microfilter and the positive resist of examples 1-10 was adjusted. The solvent indicated to Table 2 is shown below.

[0137] As a solvent, it is S1:propylene-glycol-monomethyl-ether acetate

S2:propylene-glycol-monomethyl-ether propionate S3:3-methoxy methyl propionate S4:3-ethoxy ethyl propionate S5:ethyl lactate S6:methyl-amyl-ketone S8:gamma-butyrolactone S9:propylene carbonate S10:pyruvic-acid ethyl [0138].

In this example and the example of a comparison, triphenylsulfonium triflate was used as a photo-oxide generating agent. Moreover, the positive resist was similarly adjusted using the resin (A4) compounded by the approach same as an example of a comparison as composition of a page [8th] publication of JP,10-274852,A.

[0139] (Evaluation trial) The obtained positive type photoresist liquid was applied on the silicon wafer using the spin coater, desiccation and about 0.4-micrometer ***** talent TOREJISUTO film were created for 90 seconds at 130 degrees C, and it exposed to it with the ArF excimer laser (the wavelength of 193nm, ArF stepper by the ISI company of NA=0.6). Heat-treatment after exposure was performed for 90 seconds at 120 degrees C, the rinse was carried out with development and distilled water in 2.38% of tetramethylammonium hydroxide water solution, and the resist pattern profile was obtained. About these, a development defect, edge roughness, and a dependency of condensation and rarefaction were evaluated as follows.

[0140] The [number of development defects] 6 inches Bare Each resist film was applied to 0.5 micrometers on Si substrate, and 140 degrees C dried for 60 seconds with the vacuum adsorption equation hot plate. Next, after exposing by Nikon stepper NSR-1505EX through the test mask of 0.35-micrometer contact hole pattern (Hole Duty ratio = 1:3), exposure afterbaking was performed for 90 seconds at 120 degrees C. It rinsed for 30 seconds after the paddle development for 60 seconds, and with pure water by TMAH (tetramethylammonium hydroxide water solution) 2.38% succeedingly, and spin desiccation was carried out. In this way, the primary data value measured and acquired [number / of development defects] by KLA-2112 Made from a KEERUE ten call opportunity in the obtained sample was made into the number of development defects.

[0141] [Edge roughness] Measurement of edge roughness is performed by the edge roughness of an isolated pattern using length measurement scanning electronic ***** (SEM), within a measurement monitor, the Rhine pattern edge is detected in two or more locations, and distribution (3sigma) of the variation in that detection location is made into the index of edge roughness, and it is so desirable that this value is small.

[0142] [Dependency of condensation and rarefaction] It asked for the lap range of the depth of focus which

permits 0.22micrometer**10%, respectively in Rhine and a tooth-space pattern (dense pattern) with a line breadth of 0.22 micrometers, and the isolated Rhine pattern (non-dense pattern). It is shown this being the range or that a dependency of condensation and rarefaction is so good that it is large. The above-mentioned evaluation result is shown in Table 2.

[0143]

[Table 2]

実施例	酸分解性 樹脂	溶剤 (重量比)	現像 欠陥数	レジスト厚 (nm)	疎密 依存性
1	(1)	S 1 / S 5 (80/20)	5 5	1 1	1 . 0
2	(5)	S 3 / S 5 (75/25)	6 0	1 0	0 . 8
3	(6)	S 1 / S 6 (70/30)	7 0	1 2	1 . 0
4	(8)	S 2 / S 6 (70/30)	6 5	1 2	0 . 8
5	(1 7)	S 4 / S 6 (70/30)	7 5	1 1	1 . 0
6	(2 0)	S 1 / S 8 (90/10)	8 0	1 3	1 . 0
7	(2 8)	S 1 / S 9 (90/10)	7 5	1 1	0 . 8
8	(3 8)	S 2 / S 5 (70/30)	6 5	1 0	0 . 8
9	(4 5)	S 3 / S 6 (80/20)	7 0	1 2	1 . 0
1 0	(5 4)	S 4 / S 10 (70/30)	7 5	1 1	1 . 0
比較例	(A 4)	S 1	5 0 0	2 6	0 . 4

[0144] The positive-resist constituent of this invention is in level satisfying about the all so that clearly from the result of Table 2. That is, it is suitable for the lithography using far ultraviolet rays including ArF excimer laser exposure.

[0145]

[Effect of the Invention] Especially, it is suitably applied to the light of the far-ultraviolet wavelength field of the range of 150nm - 220nm, prevention of generating of sensibility, resolving power, dry etching-proof nature, substrate adhesion and also a development defect, or edge roughness is realized, a good resist pattern profile is obtained, and the positive type photoresist constituent for far-ultraviolet-rays exposure of this invention is further excellent also in a dependency of condensation and rarefaction.

[Translation done.]